

BEST AVAILABLE COPY

# ADVANCED INORGANIC CHEMISTRY

*Fifth Edition*

---

**F. ALBERT COTTON**

W. T. DOHERTY-WELCH FOUNDATION  
DISTINGUISHED PROFESSOR OF CHEMISTRY  
TEXAS A AND M UNIVERSITY  
COLLEGE STATION, TEXAS, USA

and

**GEOFFREY WILKINSON**

SIR EDWARD FRANKLAND PROFESSOR OF INORGANIC CHEMISTRY  
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY  
UNIVERSITY OF LONDON, ENGLAND

A WILEY-INTERSCIENCE PUBLICATION

**JOHN WILEY & SONS**

New York • Chichester • Brisbane • Toronto • Singapore

... *Chemistry, the most cosmopolitan of sciences,  
the most secret of arts.*

D'Arcy Wentworth Thompson

*La Chimie crée son objet.*

Marcellin Berthelot

Copyright © 1988 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Sections 107 and 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

**Library of Congress Cataloging in Publication Data**

Cotton, F. Albert (Frank Albert), 1930-

Advanced inorganic chemistry: a comprehensive text/F. Albert Cotton and Geoffrey Wilkinson.—5th ed., completely rev. from the original literature.

p. cm.

"A Wiley-Interscience publication."

Includes bibliographies and index.

ISBN 0-471-84997-9

1. Chemistry, Inorganic. I. Wilkinson, Geoffrey, Sir, 1921-

II. Title.

QD151.2.C68 1988

546—dc19

Printed in the United States of America

10 9 8

87-20728

CIP

mic Chemistry, Prentice-Hall, Englewood

ademic Press, New York, 1979.

, Vol. 1, Pergamon Press, Oxford, 1987.

York, 1985.

ie Chemical Bond, 2nd ed., Wiley, New

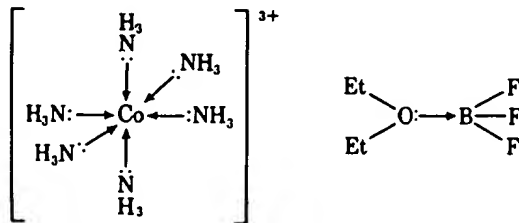
## Chapter Two

# Introduction to Ligands and Complexes

### GENERAL REMARKS

#### 2-1. Introduction

It was known long before the Danish chemist S. M. Jørgensen (1837–1914) began his extensive studies on the synthesis of such “complex” compounds that the metal halides and other salts could give compounds with neutral molecules and that many of these compounds could easily be formed in aqueous solutions. The recognition of the true nature of “complexes” began with Alfred Werner (1866–1919) as set out in his classic work *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (1905)<sup>1</sup>; he received the Nobel Prize for this work in 1913. Werner showed that neutral molecules were bound directly to the metal so that complex salts such as  $\text{CoCl}_3 \cdot 6\text{NH}_3$  were correctly formulated  $[\text{Co}(\text{NH}_3)_6]^{3+} \text{Cl}_3^-$ . He also demonstrated that there were profound stereochemical consequences of the assumption that the molecules or ions (ligands) around the metal occupied positions at the corners of an octahedron or a square. The stereochemical studies of Werner were later followed by the ideas of G. N. Lewis and N. V. Sidgwick, who proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair (Lewis base) can donate these electrons to a metal ion or other electron acceptor (Lewis acid). Well-known examples are the following:



<sup>1</sup>Braunschweig, 1905; English translation of second edition as *New Ideas on Inorganic Chemistry*, by E. P. Hedley, London, 1911.

We can now define a *ligand*\* as any molecule or ion that has at least one electron pair that can be so donated. Ligands may also be called Lewis bases; in the terms used in organic chemistry, they are nucleophiles. Metal ions or molecules such as  $\text{BF}_3$  with incomplete valence electron shells are Lewis acids or electrophiles.

Although it is possible to regard even covalent compounds from the donor-acceptor point of view—for example, we could regard methane ( $\text{CH}_4$ ) as composed of  $\text{C}^{4+}$  and four  $\text{H}^-$  ions—it is not a particularly profitable or realistic way of looking at such molecules. Nevertheless, in inorganic chemistry, ions such as  $\text{H}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , and groups such as  $\text{CH}_3^-$  and  $\text{C}_6\text{H}_5^-$ , are commonly termed ligands even when they are bound in simple molecules by largely covalent bonds as in  $\text{SF}_6$  or  $\text{W}(\text{CH}_3)_6$ . Although  $\text{SiF}_4$  is normally called a molecule and  $\text{SiF}_6^{2-}$  a complex anion, the nature of the Si—F bonds in each species is essentially the same.

There are many ways of classifying ligands. One approach is based on the type of bonding interaction between the central atom and its neighbors. The bonding details are dealt with later, but the distinction between two major types of ligand can be illustrated by posing two questions.

1. Why do molecules like water or ammonia give complexes with ions of *both* main group and transition metals—for example,  $[\text{Al}(\text{OH}_2)_6]^{3+}$  or  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , while other types of molecules such as  $\text{PF}_3$  or  $\text{CO}$  give complexes only with transition metals?

2. Although  $\text{PF}_3$  and  $\text{CO}$  give neutral complexes such as  $\text{Ni}(\text{PF}_3)_4$  or  $\text{Cr}(\text{CO})_6$ , why do  $\text{NH}_3$ , amines, oxygen compounds, and so on, not give complexes such as  $\text{Ni}(\text{NH}_3)_4$ ?

There are two main classes of ligands:

(a) *Classical or simple donor ligands* act as electron-pair donors to acceptor ions or molecules, and form complexes with all types of Lewis acids, metal ions, or molecules.

(b) *Nonclassical ligands,  $\pi$ -bonding or  $\pi$ -acid ligands*, form compounds largely if not entirely with transition metal atoms. This interaction occurs because of the special properties of both metal and ligand. The metal has *d* orbitals that can be utilized in bonding; the ligand has not only *donor* capacity but also has *acceptor* orbitals. This latter distinction is perhaps best illustrated by comparison of an amine,  $:\text{NR}_3$ , with a tertiary phosphine,  $:\text{PR}_3$ . Both can act as bases toward  $\text{H}^+$ , but the P atom differs from N in that it has vacant *3d* orbitals of low energy, whereas in N the lowest energy *d* orbitals are at far too high an energy to use. Another example is that of  $\text{CO}$ , which has no measurable basicity to protons, yet readily reacts with metals like nickel that have high heats of atomization to give compounds like  $\text{Ni}(\text{CO})_4$ .

Ligands may also be classified electronically, that is, according to the number of electrons that they contribute to a central atom when these ligands are regarded (sometimes artificially) as neutral species. Thus atoms or groups that can form a covalent bond are regarded as *one-electron* donors—examples

\*For a history of the term, see W. H. Brock *et al.*, *Polyhedron*, 1983, 2, 1.

le or ion that has at least one  
may also be called Lewis bases;  
re nucleophiles. Metal ions or  
electron shells are Lewis acids

nt compounds from the donor-  
uld regard methane ( $\text{CH}_4$ ) as  
ot a particularly profitable or  
vertheless, in inorganic chem-  
 $\text{O}_4^{2-}$ , and groups such as  $\text{CH}_3^-$   
when they are bound in simple  
or  $\text{W}(\text{CH}_3)_6$ . Although  $\text{SiF}_4$  is  
plex anion, the nature of the  
same.

One approach is based on the  
al atom and its neighbors. The  
distinction between two major  
o questions.

ia give complexes with ions of  
or example,  $[\text{Al}(\text{OH}_2)_6]^{3+}$  or  
such as  $\text{PF}_3$  or  $\text{CO}$  give com-

es such as  $\text{Ni}(\text{PF}_3)_4$  or  $\text{Cr}(\text{CO})_6$ ,  
so on, not give complexes such

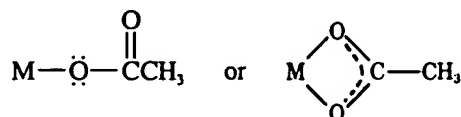
electron-pair donors to acceptor  
all types of Lewis acids, metal

acid ligands, form compounds  
atoms. This interaction occurs  
al and ligand. The metal has  $d$   
and has not only *donor* capacity  
ction is perhaps best illustrated  
iary phosphine,  $:\text{PR}_3$ . Both can  
rs from N in that it has vacant  
lowest energy  $d$  orbitals are at  
ple is that of  $\text{CO}$ , which has no  
acts with metals like nickel that  
ounds like  $\text{Ni}(\text{CO})_4$ .

y, that is, according to the num-  
ral atom when these ligands are  
species. Thus atoms or groups  
*one-electron donors*—examples

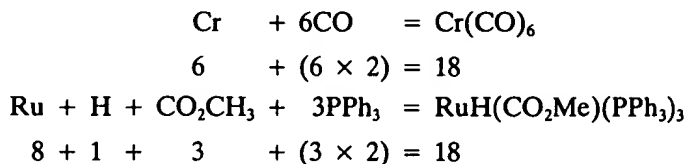
hedron, 1983, 2, 1.

are F, SH, and  $\text{CH}_3$ . Any compound with an electron pair is a *two-electron donor* (e.g.,  $:\text{NH}_3$ ,  $\text{H}_2\text{O}:$ ). Groups that can form a single bond and at the same time donate can be considered to be *three-electron donors*. For example, the acetate ion can be either a one- or a three-electron donor, namely,



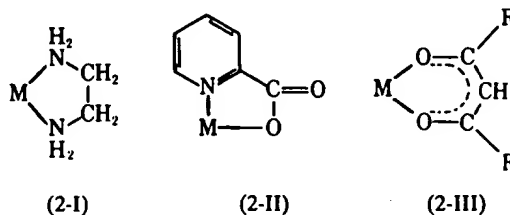
A molecule with two electron pairs (e.g.,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ) can be regarded as a *four-electron donor*, and so on. This classification method is useful in that it is an aid in electron counting, particularly for transition metal complexes whose valence shells contain 18 electrons and whose stoichiometries correspond to what is called the *18-electron rule* or noble gas formalism. This is merely a phenomenological way of expressing the tendency of a transition metal atom to use all its valence orbitals, namely, the five  $nd$ , the  $(n+1)s$ , and the three  $(n+1)p$  orbitals as fully as possible in metal-ligand bonding. The sum of the number of valence electrons in the gaseous atom plus the number of electrons from neutral ligands may attain a maximum value of 18.

This is illustrated by the following examples:



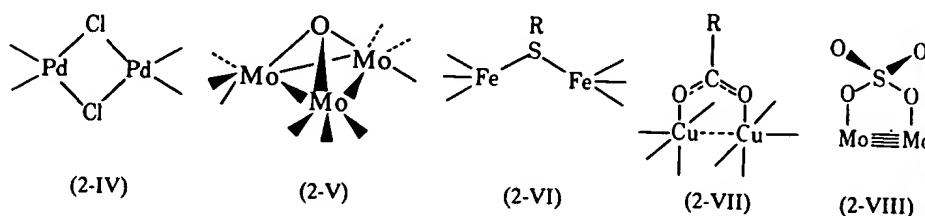
A third way of classifying ligands is *structurally*, that is, by the number of connections they make to the central atom. Where only one atom becomes closely connected (bonded) the ligand is said to be *unidentate* [e.g., the ligands in  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\text{AlCl}_4^-$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ]. When a ligand becomes attached by two or more atoms it is *bidentate*, *tridentate*, *tetradentate*, and so on, generally multidentate. Note that the Greek-derived corresponding prefixes (mono-, di-, tri-, tetra-, penta-, hexa-, etc.) are also used in the literature.

Bidentate ligands when bound entirely to one atom are termed *chelate*, as in (2-I), (2-II), and (2-III).



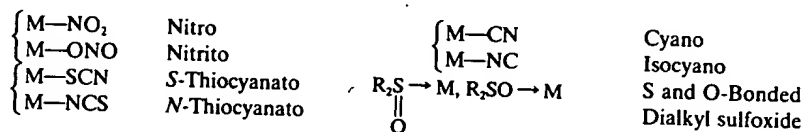
Another important role of ligands is as *bridging groups*. In many cases they serve as *unidentate* bridging ligands. This means that there is only *one*

ligand atom that forms two (or even three) bonds to different metal atoms. For monoatomic ligands, such as the halide ions, and those containing only one possible donor atom, this *unidentate* form of bridging is, of course, the only possible one. A few examples are shown in (2-IV) to (2-VI). Ligands having more than one atom that can be an electron donor often function as *bidentate* bridging ligands. Examples are shown in (2-VII) and (2-VIII).



The standard notation for bridging ligands employs the descriptors  $\eta$  (eta) and  $\mu$  (mu). The prefix  $\eta^n$  indicates that a ligand is using  $n$  of its atoms to form bonds to metal atoms ( $\eta$  is used also for nonbridging ligands, see Sections 2-10 to 2-12.), while the prefix  $\mu$  implies that a ligand bridges two metal atoms. If a ligand bridges three, four, or more metal atoms,  $\mu_3$ , or  $\mu_4$ , and so on, are used. For example, in (2-IV), the chlorine atoms are  $\mu\text{-Cl}$ , while in (2-V) the oxygen atom is  $\mu_3\text{-O}$ . In (2-VII), the carboxylato ligand is  $\mu, \eta^2$  since it bridges two metal atoms (hence  $\mu$ ) employing two different oxygen atoms (hence  $\eta^2$ ).

Some unidentate ligands have two or more different donor sites so that the possibility of *linkage isomerism* arises. Some important ligands of this type, which are called *ambidentate ligands*, are

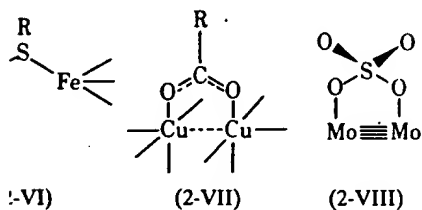


The next sections discuss primarily the chemistry of simple donor ligands. Much of this chemistry applies equally well to main group metal ions (e.g.,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ga}^{3+}$ , or  $\text{Cd}^{2+}$ ) and to transition metal ions. It is a chemistry largely of aqua ions, nitrogen donor ligands, such as ammonia or ethylenediamine, and halide ions, and it is chemistry of metal ions in positive oxidation states, usually 2+ and 3+.

Later sections consider complexes that have  $\pi$ -bonding ligands and also compounds that are called  $\pi$  complexes, which are those formed by unsaturated organic molecules. This is a chemistry largely of transition metals, often in formally low oxidation states such as -1, 0, and +1.

The borderline between  $\pi$ -bonding and non- $\pi$ -bonding ligands is by no means clearly defined. Also the terms "nonclassical" versus "classical" are

) bonds to different metal atoms. le ions, and those containing only orm of bridging is, of course, the own in (2-IV) to (2-VI). Ligands 1 electron donor often function as hown in (2-VII) and (2-VIII).



ds employs the descriptors  $\eta$  (eta) a ligand is using  $n$  of its atoms to r nonbridging ligands, see Sections : that a ligand bridges two metal more metal atoms,  $\mu_3$ , or  $\mu_4$ , and he chlorine atoms are  $\mu\text{-Cl}$ , while II), the carboxylato ligand is  $\mu, \eta^2$ ) employing two different oxygen

more different donor sites so that . Some important ligands of this , are

- |                       |                   |
|-----------------------|-------------------|
| 1—CN                  | Cyano             |
| 1—NC                  | Isocyano          |
| $R_2SO \rightarrow M$ | S and O-Bonded    |
|                       | Dialkyl sulfoxide |

chemistry of simple donor ligands. ll to main group metal ions (e.g., tion metal ions. It is a chemistry ds, such as ammonia or ethylene- of metal ions in positive oxidation

have  $\pi$ -bonding ligands and also hich are those formed by unsatu- / largely of transition metals, often 1, 0, and +1.

l non- $\pi$ -bonding ligands is by no onclassical" versus "classical" are

of limited validity, since Werner and his contemporaries studied complexes of cyanide ion and of tertiary phosphines; even pyridine, which they used extensively, is not solely a simple donor.

## STABILITY OF COMPLEX IONS IN AQUEOUS SOLUTION

### 2-2. Aqua Ions

In a fundamental sense metal ions simply dissolved in water are already complexed—they have formed aqua ions. The process of forming in aqueous solution what we more conventionally call complexes is really one of displacing one set of ligands, which happen to be water molecules, by another set. Thus the logical place to begin a discussion of the formation and stability of complex ions in aqueous solution is with the aqua ions themselves.

From thermodynamic cycles the enthalpies of plunging gaseous metal ions into water can be estimated and the results,  $2 \times 10^2$  to  $4 \times 10^3 \text{ kJ mol}^{-1}$  (see Table 2-1), show that these interactions are very strong indeed. It is of importance in understanding the behavior of metal ions in aqueous solution to know how many water molecules each of these ions binds by direct metal-oxygen bonds. To put it another way, if we regard the ion as being an aqua complex  $[M(H_2O)_x]^{n+}$ , which is then further and more loosely solvated, we wish to know the coordination number  $x$  and also the manner in which the  $x$  water molecules are arranged around the metal ion. Classical measurements of various types—for example, ion mobilities, apparent hydrated radii, entropies of hydration—fail to give such detailed information because they cannot make any explicit distinction between those water molecules directly bonded to the metal—the  $x$  water molecules in the inner coordination sphere—and additional molecules that are held less strongly by hydrogen bonds to the water molecules of the inner coordination sphere. There are, however, ways of answering the question in many instances, ways depending, for the most

TABLE 2-1  
Enthalpies of Hydration\* of Some Ions ( $\text{kJ mol}^{-1}$ )

H <sup>+</sup>	-1091	Ca <sup>2+</sup>	-1577	Cd <sup>2+</sup>	-1807
Li <sup>+</sup>	-519	Sr <sup>2+</sup>	-1443	Hg <sup>2+</sup>	-1824
Na <sup>+</sup>	-406	Ba <sup>2+</sup>	-1305	Sn <sup>2+</sup>	-1552
K <sup>+</sup>	-322	Cr <sup>2+</sup>	-1904	Pb <sup>2+</sup>	-1481
Rb <sup>+</sup>	-293	Mn <sup>2+</sup>	-1841	Al <sup>3+</sup>	-4665
Cs <sup>+</sup>	-264	Fe <sup>2+</sup>	-1946	Fe <sup>3+</sup>	-4430
Ag <sup>+</sup>	-473	Co <sup>2+</sup>	-1996	F <sup>-</sup>	-515
Tl <sup>+</sup>	-326	Ni <sup>2+</sup>	-2105	Cl <sup>-</sup>	-381
Be <sup>2+</sup>	-2494	Cu <sup>2+</sup>	-2100	Br <sup>-</sup>	-347
Mg <sup>2+</sup>	-1921	Zn <sup>2+</sup>	-2046	I <sup>-</sup>	-305

\*Absolute values are based on the assignment of  $-1091 \pm 10 \text{ kJ mol}^{-1}$  to H<sup>+</sup> (cf. H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, 1963, 59, 1126). Each value probably has an uncertainty of at least  $10n \text{ kJ mol}^{-1}$ , where  $n$  is the charge of the ion.

part, on modern physical and theoretical developments. A few illustrative examples will be considered here.

For the transition metal ions, the spectral and, to a lesser degree, magnetic properties depend on the constitution and symmetry of their surroundings. For example, the  $\text{Co}^{\text{II}}$  ion forms both octahedral and tetrahedral complexes. Thus we might suppose that the aqua ion could be either  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  with octahedral symmetry, or  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  with tetrahedral symmetry. It is found that the spectrum and the magnetism of  $\text{Co}^{\text{II}}$  in pink aqueous solutions of its salts with noncoordinating anions such as  $\text{ClO}_4^-$  or  $\text{NO}_3^-$  are very similar to the corresponding properties of octahedrally coordinated  $\text{Co}^{\text{II}}$  in general, and virtually identical with those of  $\text{Co}^{\text{II}}$  in such hydrated salts as  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  where from X-ray studies octahedral  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions definitely exist. Complementing this, the spectral and magnetic properties of the many known tetrahedral  $\text{Co}^{\text{II}}$  complexes, such as  $[\text{CoCl}_4]^{2-}$ ,  $[\text{CoBr}_4]^{2-}$ ,  $[\text{Co}(\text{NCS})_4]^{2-}$ , and  $[\text{py}_2\text{CoCl}_2]$ , which are intensely green, blue, or purple, are completely different from those of  $\text{Co}^{\text{II}}$  in aqueous solution. Thus there is little doubt that aqueous solutions of otherwise uncomplexed  $\text{Co}^{\text{II}}$  contain predominantly\* well-defined, octahedral  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions, further hydrated, of course. Evidence of similar character can be adduced for many of the other transitional metal ions. For all the di- and tripositive ions of the first transition series, the aqua ions are octahedral  $[\text{M}(\text{H}_2\text{O})_6]^{2(\text{or } 3)+}$  species, although in those of  $\text{Cr}^{\text{II}}$ ,  $\text{Mn}^{\text{III}}$ , and  $\text{Cu}^{\text{II}}$  there are definite distortions of the octahedra because of the Jahn-Teller effect.† Information on aqua ions of the second and third transition series, of which there are only a few, however, is not so certain. It is probable that the coordination is octahedral in many, but higher coordination numbers may occur. For the lanthanide ions,  $\text{M}^{3+}(\text{aq})$ , it is certain that the coordination number is higher.

For ions that do not have partly filled  $d$  shells, evidence of the kind mentioned is lacking, since such ions do not have spectral or magnetic properties related in a straightforward way to the nature of their coordination spheres. We are therefore not sure about the state of aquation of many such ions, although nmr and other relaxation techniques have now supplied some such information. It should be noted that, even when the existence of a well-defined aqua ion is certain, there are vast differences in the average length of time that a water molecule spends in the coordination sphere, the so-called mean residence time. For  $\text{Cr}^{\text{III}}$  and  $\text{Rh}^{\text{III}}$  this time is so long that when a solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  in ordinary water is mixed with water enriched in  $^{18}\text{O}$ , many hours are required for complete equilibration of the enriched solvent water with the coordinated water. From a measurement of how many molecules of  $\text{H}_2\text{O}$  in the  $\text{Cr}^{\text{III}}$  and  $\text{Rh}^{\text{III}}$  solutions fail immediately to exchange with the enriched water added, the coordination numbers of these ions by water were shown to be 6. These cases are exceptional, however. Most other

\*However, there are also *small* quantities of tetrahedral  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ ; see T. J. Swift, *Inorg. Chem.*, 1964, 3, 526.

†This effect requires molecules to adopt geometries that do not lead to a degeneracy in valence level orbitals.



developments. A few illustrative

al and, to a lesser degree, magnetic  
l symmetry of their surroundings.  
hedral and tetrahedral complexes.  
could be either  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  with  
h tetrahedral symmetry. It is found  
o<sup>II</sup> in pink aqueous solutions of its  
 $\text{ClO}_4^-$  or  $\text{NO}_3^-$  are very similar to  
ly coordinated  $\text{Co}^{II}$  in general, and  
uch hydrated salts as  $\text{Co}(\text{ClO}_4)_2 \cdot$   
studies octahedral  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$   
he spectral and magnetic properties  
exes, such as  $[\text{CoCl}_4]^{2-}$ ,  $[\text{CoBr}_4]^{2-}$ ,  
intensely green, blue, or purple,  
<sup>II</sup> in aqueous solution. Thus there  
herwise uncomplexed  $\text{Co}^{II}$  contain

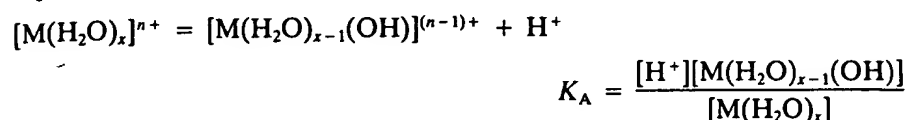
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ions, further hy-  
racter can be adduced for many of  
the di- and tripositive ions of the  
ahedral  $[\text{M}(\text{H}_2\text{O})_6]^{2(\text{or } 3)+}$  species,  
here are definite distortions of the  
ect.† Information on aqua ions of  
rich there are only a few, however,  
ordination is octahedral in many,  
For the lanthanide ions,  $\text{M}^{3+}(\text{aq})$ ,  
is higher.

l shells, evidence of the kind men-  
ve spectral or magnetic properties  
ture of their coordination spheres.  
e of aquation of many such ions,  
ques have now supplied some such  
en when the existence of a well-  
t differences in the average length  
coordination sphere, the so-called  
this time is so long that when a  
r is mixed with water enriched in  
lete equilibration of the enriched  
From a measurement of how many  
tions fail immediately to exchange  
ination numbers of these ions by  
exceptional, however. Most other  
edra  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ; see T. J. Swift, *Inorg.*

that do not lead to a degeneracy in valence

aqua ions are far more labile, and a similar equilibration would occur too rapidly to permit the same type of measurement. This particular rate problem is only one of several that are discussed more fully in Section 29-3.

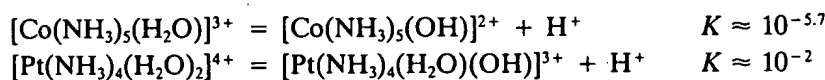
Aqua ions are all more or less acidic; that is, they dissociate in a manner represented by the equation



The acidities vary widely, as the following  $K_A$  values show:

M in $[\text{M}(\text{H}_2\text{O})_6]^{n+}$	$K_A$
$\text{Al}^{III}$	$1.12 \times 10^{-5}$
$\text{Cr}^{III}$	$1.26 \times 10^{-4}$
$\text{Fe}^{III}$	$6.3 \times 10^{-3}$

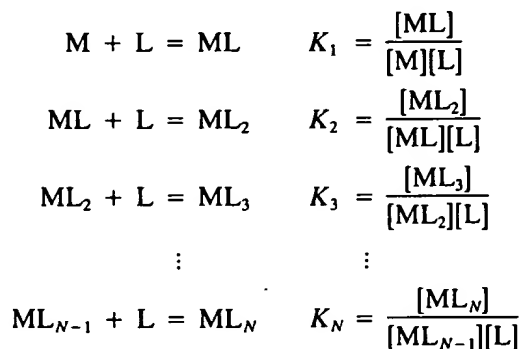
Coordinated water molecules in other complexes also dissociate in the same way, for example,



### 2-3. Formation Constants of Complexes

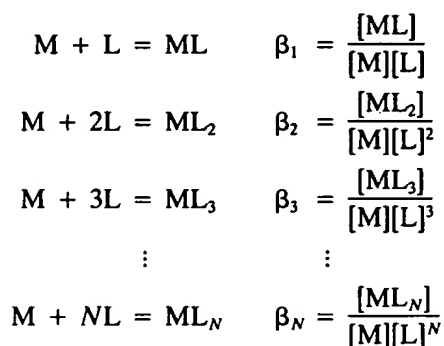
The thermodynamic stability of a complex can be indicated by an equilibrium constant relating its concentration to the concentration of other species *when the system has reached equilibrium*. The kinetic stability of a species refers to the speed with which transformations leading to the attainment of equilibrium will occur. This section considers problems of thermodynamic stability, that is, the nature of equilibria once they are established.

If in a solution containing aquated metal ions M and unidentate ligands L, only soluble mononuclear complexes are formed, the system at equilibrium may be described by the following equations and equilibrium constants:



There will be  $N$  such equilibria, where  $N$  represents the maximum coordination number of the metal ion  $M$  for the ligand  $L$ , and  $N$  may vary from one ligand to another. For instance,  $Al^{3+}$  forms  $AlCl_4^-$  and  $AlF_6^{3-}$  and  $Co^{2+}$  forms  $CoCl_4^{2-}$  and  $Co(NH_3)_6^{2+}$ , as the highest complexes with the ligands indicated.

Another way of expressing the equilibrium relations follows:



Since there can be only  $N$  independent equilibria in such a system, it is clear that the  $K_i$ 's and the  $\beta_i$ 's must be related. The relationship is indeed rather obvious. Consider, for example, the expression for  $\beta_3$ . Let us multiply both numerator and denominator by  $[ML][ML_2]$  and then rearrange slightly:

$$\begin{aligned}
 \beta_3 &= \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \\
 &= \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]}
 \end{aligned}$$

It is not difficult to see that this kind of relationship is perfectly general, namely,

$$\beta_k = K_1 K_2 K_3 \cdots K_k = \prod_{i=1}^{i=k} K_i$$

The  $K_i$ 's are called the *stepwise formation constants* (or stepwise stability constants), and the  $\beta_i$ 's are called the *overall formation constants* (or overall stability constants); each type has its special convenience in certain cases.

In all of the previous equilibria we have written the metal ion without specifying charge or degree of solvation. The former omission is obviously of no importance, for the equilibria may be expressed as above whatever the charges. Omission of the water molecules is a convention that is usually convenient and harmless. It must be remembered when necessary. See, for example, the discussion of the chelate effect, in the next section.

With only a few exceptions, there is generally a slowly descending progression in the values of the  $K_i$ 's in any particular system. This is illustrated

represents the maximum coordination of ligand L, and N may vary from 1 to 6 for  $\text{AlCl}_4^-$  and  $\text{AlF}_6^{3-}$  and  $\text{Co}^{2+}$  forms complexes with the ligands indicated.

The following relations follow:

$$\alpha_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]}$$

$$\alpha_2 = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2}$$

$$\alpha_3 = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3}$$

$$\vdots$$

$$\alpha_N = \frac{[\text{ML}_N]}{[\text{M}][\text{L}]^N}$$

In equilibria in such a system, it is clear that the relationship is indeed rather simple for  $\beta_3$ . Let us multiply both sides of the equation and then rearrange slightly:

$$\frac{[\text{ML}_2]}{[\text{ML}_2]} \cdot \frac{[\text{ML}_3]}{[\text{ML}_2][\text{L}]}$$

This relationship is perfectly general,

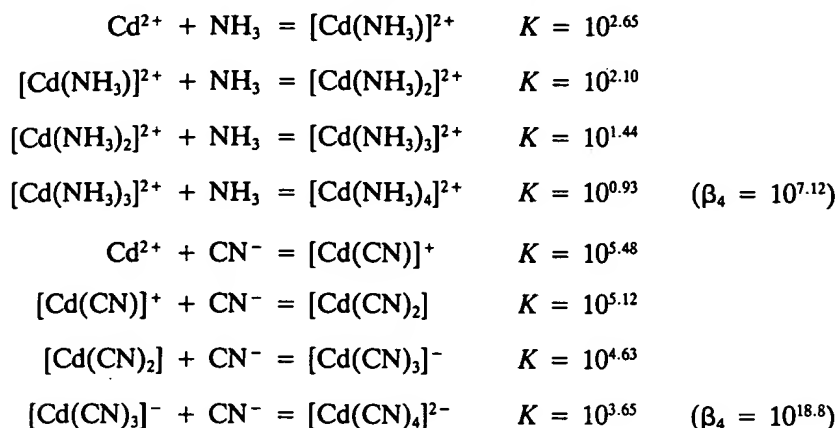
$$\alpha_i = \prod_{j=1}^{i-1} K_j$$

where  $K_i$  are the stepwise stability constants (or stepwise stability formation constants) (or overall formation constants in certain cases).

When written the metal ion without the former omission is obviously expressed as above whatever the value of i is a convention that is usually observed when necessary. See, for example, in the next section.

Generally a slowly descending proportion of the various complexes in a particular system. This is illustrated

by the data for the  $\text{Cd}^{II}-\text{NH}_3$  system where the ligands are uncharged and by the  $\text{Cd}^{II}-\text{CN}^-$  system where the ligands are charged.



Thus, typically, as ligand is added to the solution of metal ion, ML is first formed more rapidly than any other complex in the series. As addition of ligand is continued, the  $\text{ML}_2$  concentration rises rapidly, while the ML concentration drops, then  $\text{ML}_3$  becomes dominant, ML and  $\text{ML}_2$  becoming unimportant, and so forth, until the highest complex  $\text{ML}_N$  is formed, to the nearly complete exclusion of all others at very high ligand concentrations. These relationships are conveniently displayed in diagrams such as those shown in Fig. 2-1.

A steady decrease in  $K_i$  values with increasing i is to be expected, provided there are only slight changes in the metal-ligand bond energies as a function of i, which is usually the case. For example, in the  $\text{Ni}^{2+}-\text{NH}_3$  system to be discussed next, the enthalpies of the successive reactions  $\text{Ni}(\text{NH}_3)_{i-1} + \text{NH}_3 = \text{Ni}(\text{NH}_3)_i$  are all within the range 16.7 to 18.0  $\text{kJ mol}^{-1}$ .

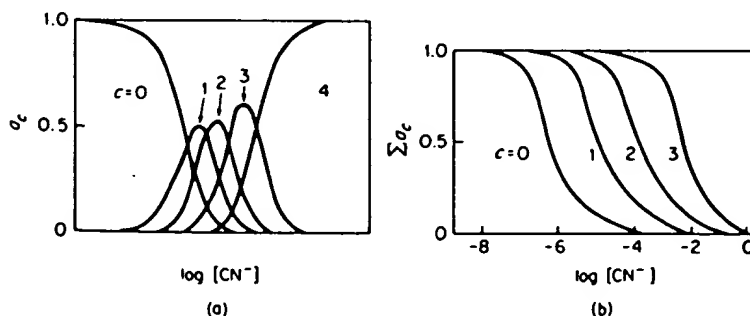


FIG. 2-1. Plots of the proportions of the various complexes  $[\text{Cd}(\text{CN})_i]^{(2-i)+}$  as a function of the ligand concentration.

$$\alpha_i = [\text{Cd}(\text{CN})_i] / \text{total Cd} \quad \Sigma \alpha_i = \sum_{i=0}^4 [\text{Cd}(\text{CN})_i] / \text{total Cd}$$

[Reproduced by permission from F. J. C. Rossetti, in *Modern Coordination Chemistry*, J. Lewis and R. G. Wilkins, Eds., Interscience, 1960, p. 10.

There are several reasons for a steady decrease in  $K_i$  values as the number of ligands increases: (1) statistical factors, (2) increased steric hindrance as the number of ligands increases if they are bulkier than the  $H_2O$  molecules they replace, (3) Coulombic factors, mainly in complexes with charged ligands. The statistical factors may be treated in the following way.<sup>2</sup> Suppose, as is almost certainly the case for  $Ni^{2+}$ , that the coordination number remains the same throughout the series  $[M(H_2O)_N] \cdots [M(H_2O)_{N-n}L_n] \cdots [ML_N]$ . The  $[M(H_2O)_{N-n}L_n]$  species has  $n$  sites from which to lose a ligand, whereas the species  $[M(H_2O)_{N-n+1}L_{n-1}]$  has  $(N - n + 1)$  sites at which to gain a ligand. Thus the relative probability of passing from  $[M(H_2O)_{N-n+1}L_{n-1}]$  to  $[M(H_2O)_{N-n}L_n]$  is proportional to  $(N - n + 1)/n$ . Similarly, the relative probability of passing from  $[M(H_2O)_{N-n}L_n]$  to  $[M(H_2O)_{N-n-1}L_{n+1}]$  is proportional to  $(N - n)/(n + 1)$ . Hence on the basis of these statistical considerations alone, we expect

$$K_{n+1}/K_n = \frac{N - n}{n + 1} \div \frac{N - n + 1}{n} = \frac{n(N - n)}{(n + 1)(N - n + 1)}$$

In the  $Ni^{2+}-NH_3$  system ( $N = 6$ ), we find the comparison between experimental ratios of successive constants and those calculated from the previous formula to be as shown in Table 2-2. The experimental ratios are consistently smaller than the statistically expected ones, which is typical and shows that other factors are also of importance.

There are cases where the experimental ratios of the constants do not remain constant or change monotonically; instead, one of them is singularly large or small. There are several reasons for this: (1) an abrupt change in coordination number and hybridization at some stage of the sequence of complexes, (2) special steric effects that become operative only at a certain stage of coordination, and (3) an abrupt change in electronic structure of the metal ion at a certain stage of complexation. Each of these is now illustrated.

Values of  $K_3/K_2$  are anomalously low for the halogeno complexes of mercury (II);  $HgX_2$  species are linear, whereas  $[HgX_4]^{2+}$  species are tetrahedral. Presumably the change from  $sp$  to  $sp^3$  hybridization occurs on going from

TABLE 2-2  
Comparison of Experimental and Statistical Formation  
Constants of  $Ni^{2+}-NH_3$  Complexes

	Experimental	Statistical
$K_2/K_1$	0.28	0.417
$K_3/K_2$	0.31	0.533
$K_4/K_3$	0.29	0.562
$K_5/K_4$	0.36	0.533
$K_6/K_5$	0.2	0.417

<sup>2</sup>For a more elaborate discussion see R. Pizér, *Inorg. Chem.*, 1984, 23, 3027.

ease in  $K_i$  values as the number of increased steric hindrance as bulkier than the  $H_2O$  molecules in complexes with charged ligands in the following way.<sup>2</sup> Suppose, the coordination number remains  $[M(H_2O)_{N-n}L_n] \cdots [ML_N]$ . The tendency to lose a ligand, whereas the sites at which to gain a ligand. from  $[M(H_2O)_{N-n+1}L_{n-1}]$  to  $(n+1)/n$ . Similarly, the relative to  $[M(H_2O)_{N-n-1}L_{n+1}]$  is proportional to the basis of these statistical con-

$$\frac{n(N-n)}{(n+1)(N-n+1)}$$

the comparison between experimental ratios are consistent, which is typical and shows

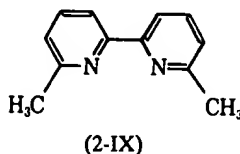
ratios of the constants do not lead, one of them is singularly this: (1) an abrupt change in some stage of the sequence of the operative only at a certain change in electronic structure of the each of these is now illustrated. The halogeno complexes of mercury  $HgX_4^{2+}$  species are tetrahedral. The change occurs on going from

Statistical Formation  
Complexes

Statistical
0.417
0.533
0.562
0.533
0.417

$HgX_2$  to  $[HgX_3]^-$ .  $K_3/K_2$  is anomalously small for the ethylenediamine complexes of  $Zn^{II}$ , and this is believed to be due to the change from tetrahedral to octahedral coordination if it is assumed that  $[Zn en_2]^{2+}$  is tetrahedral. For the  $Ag^+-NH_3$  system  $K_2 > K_1$ , indicating that the linear structure is probably attained with  $[Ag(NH_3)_2]^+$  but not with  $[Ag(NH_3)(H_2O)_{3(or 5)}]^+$ .

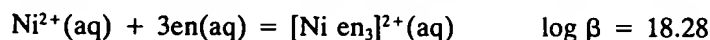
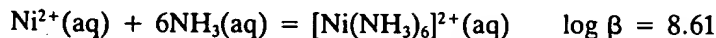
With 6,6'-dimethyl-2,2'-bipyridine (2-IX), many metal ions that form tris-2,2'-bipyridine complexes form only bis or mono complexes, or, in some cases, no isolable complexes at all, because of the steric hindrance between the methyl groups and other ligands attached to the ion.



In the series of complexes of  $Fe^{II}$  with 1,10-phenanthroline (and also with 2,2'-bipyridine),  $K_3$  is greater than  $K_2$ . This is because the tris complex is diamagnetic (i.e., the  $Fe^{2+}$  ion has the low-spin state  $t_{2g}^6$ ) whereas in the mono and bis complexes, as in the aqua ion, there are four unpaired electrons. This change from the  $t_{2g}^4 e_g^2$  to the  $t_{2g}^6$  causes the enthalpy change for addition of the third ligand to be anomalously large because the  $e_g$  electrons are antibonding.

#### 2-4. The Chelate and Macrocyclic Effects<sup>3</sup>

The term "chelate effect" refers to the enhanced stability of a complex system containing chelate rings as compared to the stability of a system that is as similar as possible but contains none or fewer rings. As an example, consider the following equilibrium constants:



The system  $[Ni en_3]^{2+}$  in which three chelate rings are formed is nearly  $10^{10}$  times as stable as that in which no such ring is formed. Although the effect is not always so pronounced, such a chelate effect is a very general one.

To understand this effect, we must invoke the thermodynamic relationships:

$$\Delta G^\circ = -RT \ln \beta$$

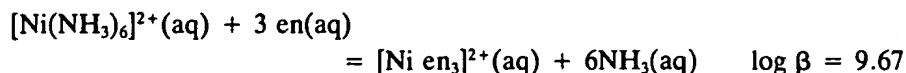
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thus  $\beta$  increases as  $\Delta G^\circ$  becomes more negative. A more negative  $\Delta G^\circ$  can result from making  $\Delta H^\circ$  more negative or from making  $\Delta S^\circ$  more positive.

<sup>3</sup>J. J. R. Frausto da Silva, *J. Chem. Educ.*, 1983, 60, 390.

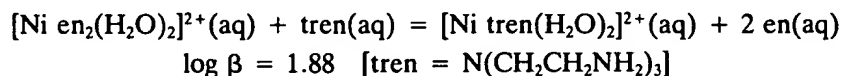
As a very simple case, consider the reactions, and the pertinent thermodynamic data for them, given in Table 2-3. In this case the enthalpy difference is well within experimental error; the chelate effect can thus be traced entirely to the entropy difference.

In the example first cited, the enthalpies make a slight favorable contribution, but the main source of the chelate effect is still to be found in the entropies. We may look at this case in terms of the following metathesis:



for which the enthalpy change is  $-12.1 \text{ kJ mol}^{-1}$ , whereas  $-T\Delta S^\circ = -43.0 \text{ kJ mol}^{-1}$ . The enthalpy change corresponds very closely to that expected from the increased crystal field stabilization energy of  $[\text{Ni en}_3]^{2+}$ , which is estimated from spectral data to be  $-11.5 \text{ kJ mol}^{-1}$  and can presumably be so explained.

As a final example, which illustrates the existence of a chelate effect despite an unfavorable enthalpy term, we may use the reaction



For this reaction we have  $\Delta H^\circ = +13.0$ ,  $-T\Delta S^\circ = -23.7$ , and  $\Delta G^\circ = -10.7$  (all in  $\text{kJ mol}^{-1}$ ). The positive enthalpy change can be attributed both to greater steric strain resulting from the presence of three fused chelate rings in Ni tren, and to the inherently weaker M—N bond when N is a tertiary rather than a primary nitrogen atom. Nevertheless, the greater number of chelate rings (3 vs. 2) leads to greater stability, owing to an entropy effect that is only partially canceled by the unfavorable enthalpy change.

Probably the main cause of the large entropy increase in each of the three cases we have been considering is the net increase in the number of unbound molecules—ligands *per se* or water molecules. Thus although 6  $\text{NH}_3$  displace 6  $\text{H}_2\text{O}$ , making no net change in the number of independent molecules, it takes only 3 en molecules to displace 6  $\text{H}_2\text{O}$ . Another more pictorial way to look at the problem is to visualize a chelate ligand with one end attached to the metal ion.<sup>4</sup> The other end cannot then get very far away, and the prob-

TABLE 2-3  
Two Reactions Illustrating a Purely Entropy-Based Chelate Effect

$\text{Cd}^{2+}(\text{aq}) + 4\text{CH}_3\text{NH}_2(\text{aq}) = [\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}(\text{aq}) \quad \log \beta = 6.52$				
$\text{Cd}^{2+}(\text{aq}) + 2\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2(\text{aq}) = [\text{Cd}(\text{en})_2]^{2+}(\text{aq}) \quad \log \beta = 10.6$				
Ligands	$\Delta H^\circ (\text{kJ mol}^{-1})$	$\Delta S^\circ (\text{J mol}^{-1} \text{ deg}^{-1})$	$-T\Delta S^\circ (\text{kJ mol}^{-1})$	$\Delta G^\circ (\text{kJ mol}^{-1})$
4 $\text{CH}_3\text{NH}_2$	-57.3	-67.3	20.1	-37.2
2 en	-56.5	+14.1	-4.2	-60.7

<sup>4</sup>D. R. Rosseinsky, *J. Chem. Soc. Dalton Trans.*, 1979, 732.

ctions, and the pertinent thermo-  
in this case the enthalpy difference  
e effect can thus be traced entirely  
s make a slight favorable contri-  
e effect is still to be found in the  
ns of the following metathesis:

q) + 6NH<sub>3</sub>(aq)    log β = 9.67  
mol<sup>-1</sup>, whereas -TΔS° = -43.0  
very closely to that expected from  
y of [Ni en<sub>3</sub>]<sup>2+</sup>, which is estimated  
l can presumably be so explained.  
xistence of a chelate effect despite  
the reaction

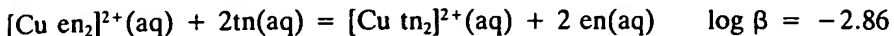
tren(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>(aq) + 2 en(aq)  
(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>]  
-TΔS° = -23.7, and ΔG° =  
lpy change can be attributed both  
esence of three fused chelate rings  
M—N bond when N is a tertiary  
ertheless, the greater number of  
ility, owing to an entropy effect  
orable enthalpy change.

ropy increase in each of the three  
crease in the number of unbound  
es. Thus although 6 NH<sub>3</sub> displace  
ber of independent molecules, it  
). Another more pictorial way to  
ligand with one end attached to  
get very far away, and the prob-

Entropy-Based Chelate Effect		
CH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> (aq)	log β = 6.52	
(en) <sub>3</sub> ] <sup>2+</sup> (aq)	log β = 10.6	
-TΔS° (kJ mol <sup>-1</sup> )	ΔG° (kJ mol <sup>-1</sup> )	
20.1	-37.2	
-4.2	-60.7	

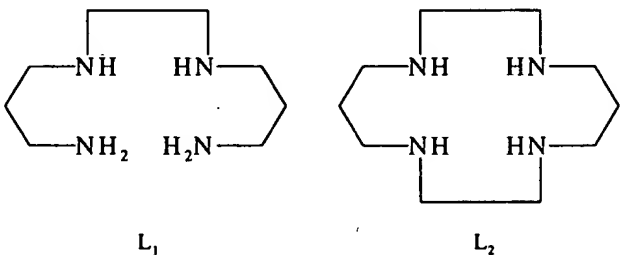
ability of it, too, becoming attached to the metal atom is greater than if this other end were instead another independent molecule, which would have access to a much larger volume of the solution.

The latter view provides an explanation for the decreasing magnitude of the chelate effect with increasing ring size, as illustrated by data such as those shown below for copper complexes of H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> and H<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>(tn):



Of course, when the ring that must be formed becomes sufficiently large (seven membered or more), it becomes more probable that the other end of the chelate molecule will contact another metal ion than that it will come around to the first one and complete the ring. Table 2-4 summarizes the factors influencing the stabilities of complexes.

**The Macrocyclic Effect.** This term refers to the greater thermodynamic stability of a complex with a cyclic polydentate ligand when compared to the complex formed by a comparable noncyclic ligand. A representative comparison would be between the following pair:



The formation of zinc (II) complexes by these two ligands, that is, the reactions (2-1) have been shown<sup>5</sup> to have the following thermodynamic



parameters:

	L <sub>1</sub>	L <sub>2</sub>
log K	11.25	15.34
-ΔH° (kJ mol <sup>-1</sup> )	44.4	61.9
ΔS° (J deg <sup>-1</sup> mol <sup>-1</sup> )	66.5	85.8

The gross macrocyclic effect is evident in the increase of 4.09 units in log K. It can be seen that the overall effect is of both enthalpic and entropic origin. The relative importance of these two contributions varies from case

<sup>5</sup>M. Micheloni and P. Paoletti, *Inorg. Chim. Acta*, 1980, 43, 109.

TABLE 2-4  
Factors Influencing Solution Stability of Complexes\*

Enthalpy effects	Entropy effects
Variation of bond strength with electronegativities of metal ions and ligand donor atoms	Number of chelate rings Size of chelate ring
Ligand field effects	Changes of solvation on complex formation
Steric and electrostatic repulsion between ligands in complex	Arrangement of chelate rings
Enthalpy effects related to conformation of uncoordinated ligand	Entropy variations in uncoordinated ligands
Other Coulombic forces involving chelate ring formation	Effects resulting from differences in configurational entropies of the ligand in complex compound
Enthalpy of solution of ligands	Entropy of solution of ligands
Change in bond strength when ligand is charged (same donor and acceptor atom)	Entropy of solution of coordinated metal ions

\*From R. T. Meyers, *Inorg. Chem.*, 1978, 17, 952.

to case (see ref. 5 for a selection of comparisons), with enthalpy more often providing the dominant contribution.

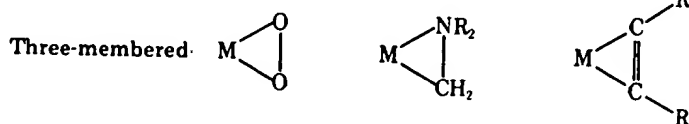
Cryptate ligands afford a similar enhancement of stability in some cases, but the availability of many ligand conformations makes this a much more complicated situation.<sup>6</sup> Some cryptate selectivity effects for alkali and alkaline earth metal ions are mentioned in Chapters 4 and 5.

## TYPES AND CLASSIFICATION OF LIGANDS

### 2-5. Multi- or Polydentate Ligands

Regardless of whether  $\pi$ -bonding is involved, ligands can have various denticities, and we now illustrate some of the more important types.

**Bidentate Ligands.** These are very common and can be classified according to the size of the chelate ring formed as in the following examples:



<sup>6</sup>H.-J. Buschmann, *Inorg. Chim. Acta*, 1985, 98, 43; 1985, 102, 95.



## Entropy effects

umber of chelate rings  
ze of chelate ring

anges of solvation on complex  
formation  
rrangement of chelate rings

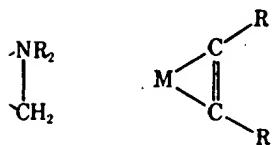
entropy variations in uncoordinated  
ligands  
ffects resulting from differences in  
configurational entropies of the ligand  
in complex compound  
entropy of solution of ligands  
entropy of solution of coordinated  
metal ions

ons), with enthalpy more often

nent of stability in some cases,  
ations makes this a much more  
ity effects for alkali and alkaline  
t and 5.

## ON OF LIGANDS

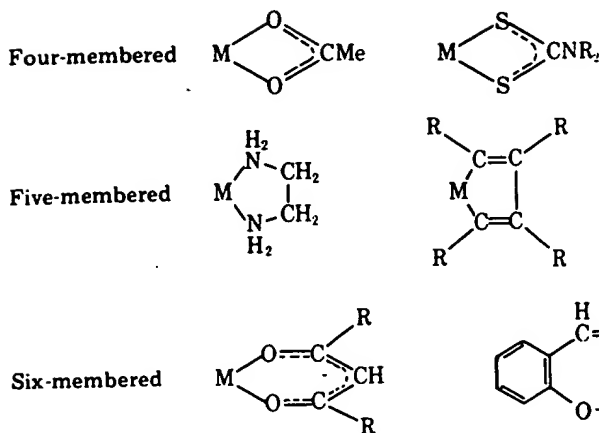
, ligands can have various den-  
re important types.  
mon and can be classified ac-  
l as in the following examples:



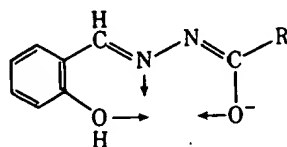
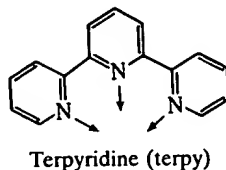
5, 102, 95.

## INTRODUCTION TO LIGANDS AND COMPLEXES

49

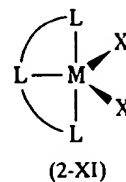
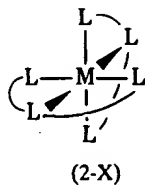


**Tridentate Ligands.** Some are *obligate planar* such as

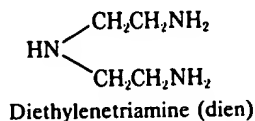


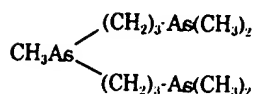
Acylhydrazones of salicylaldehyde

and many similar ones where maintenance of the  $\pi$  conjugation markedly favors planarity. Such ligands must form complexes of the types (2-X) or (2-XI).



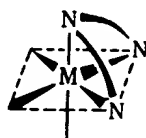
There are also many flexible tridentate ligands such as





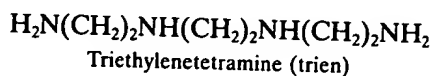
Bis(3-dimethylarsinylpropyl)methylarsine (triars)

which are about equally capable of meridional (2-X and 2-XI) and facial (2-XII) coordination.

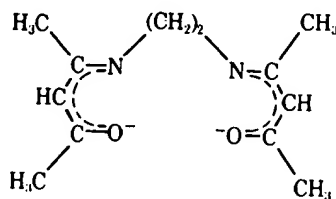


(2-XII)

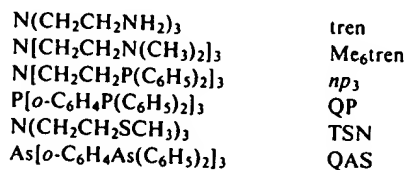
**Quadridentate Ligands.** There are four main types:  
*Open-Chain, Unbranched*



*Schiff bases* derived from acetylacetone, for example,



**Tripod Ligands.** These are of the type  $\text{X}(\text{---Y})_3$ , where X is nitrogen, phosphorus, or arsenic, the Y groups are  $\text{R}_2\text{N}$ ,  $\text{R}_2\text{P}$ ,  $\text{R}_2\text{As}$ ,  $\text{RS}$ , or  $\text{RSe}$ , and the connecting chains (---) are  $(\text{CH}_2)_2$ ,  $(\text{CH}_2)_3$ , or *o*-phenylene. Some common ones are



The tripod ligands are used particularly to favor formation of trigonal-bipyramidal complexes of divalent metal ions, as shown schematically in (2-XIII), but they do not invariably give this result. For instance, whereas  $\text{Ni}(np_3)\text{I}_2$  is trigonal-bipyramidal,  $\text{Co}(np_3)\text{I}_2$  is square pyramidal (2-XIV).

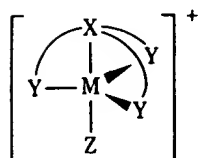
*Macrocyclic*  
phyrin (2-X)  
(Section 10  
atoms, or (2-XVI)

**Pentadentate ligands**  
pentadentate

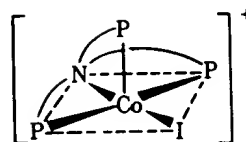
$\text{---OOCCH}$

$\text{---OOCCH}$

**Other im**  
These are complexes with mononuclear systems. The nomenclature is used, in which 15-C-5 are rules for the are known as

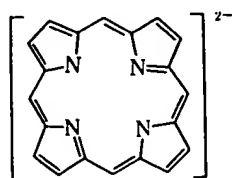


(2-XIII)

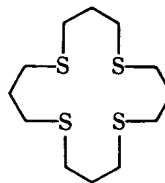


(2-XIV)

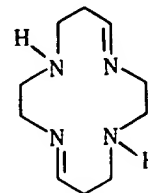
**Macrocyclic.** These may be (a) planar with unsaturated rings as in porphyrin (2-XV) and its derivatives, although, as discussed later in more detail (Section 10-12) the metal atom may be out of the plane of the nitrogen donor atoms, or (b) puckered with saturated rings as in the macrocycles (2-XVI) and (2-XVII).



(2-XV)

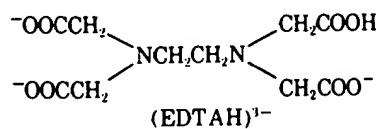
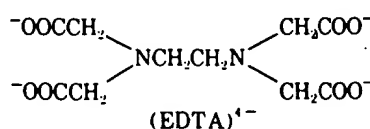


(2-XVI)

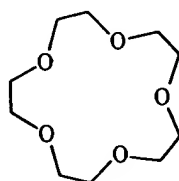


(2-XVII)

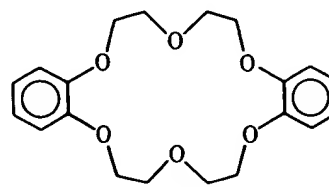
**Pentadentate and Higher-Dentate Ligands.** Perhaps the best known hexadentate ligand is ethylenediaminetetraacetate ( $\text{EDTA}^{4-}$ ), which can also be pentadentate as  $\text{EDTAH}^{3-}$ .



Other important multidentate ligands are the *crown ethers* and *cryptates*. These are cyclic and polycyclic ligands that form their most important complexes with alkali and alkaline earth ions. The macrocyclic polyethers, commonly called *crown ethers*, are typified by (2-XVIII) and (2-XIX). Since the systematic names for such ligands are very unwieldy, a special nomenclature is used, in which (2-XVIII) and (2-XIX) are called, respectively, 15-crown-5 or 15-C-5 and dibenzo-18-crown-6. These examples should serve to show the rules for the simple nomenclature. Crown ethers with as many as 10 oxygens are known and several [e.g., (2-XIX)] are commercially available.

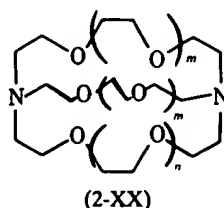


(2-XVIII)



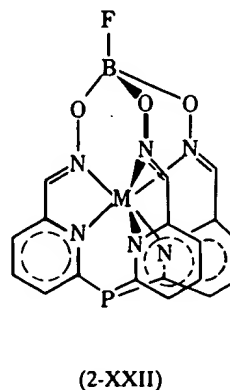
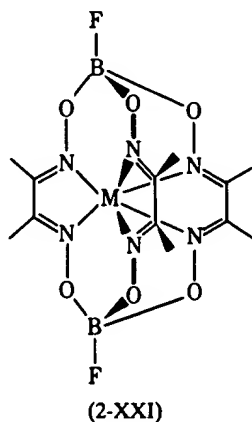
(2-XIX)

The cryptates are bicyclic species, most of which have the general formula (2-XX). Again a simplified code for naming them is a practical necessity. They are called "cryptate-*mmn*," where *m* and *n* are as defined in (2-XX). One of the commonest is cryptate-222.



These ligands have two characteristics that make them unusually interesting. Because they are chelating ligands of high denticity they give very high formation constants, and since the size of ion that will best fit the cavities can be predetermined by changing the ring size, these ligands can be designed to be selective.

In addition to the cryptates, which are synthesized apart from metal ions and then used to form complexes, there are other types of multicyclic ligand called *encapsulating ligands*, which are synthesized around the metal ion and cannot release it. Two of these are (2-XXI) and (2-XXII). An encapsulation complex allows studies to be carried out under extremely acidic or basic conditions since the metal ion, though it cannot be removed, can be oxidized or reduced. Such ligands also can enforce unusual coordination geometries; in the examples shown the coordination is much closer to trigonal prismatic than to octahedral.



**Ligands of Unusual Reach.** Ordinarily bidentate ligands occupy cis positions around a metal ion. This is because two potential donor atoms separated by a chain long enough to be able to span two trans positions would

have a  
form on  
to coord  
inorgani  
thesizing  
the don  
plex or  
(2-XXII  
can be  
R<sub>2</sub>P(CH

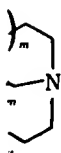
## 2-6. C

Simple  
are adeq  
complex  
and cer  
can be  
formati  
formed

Figur  
the abs  
figure, t  
therefor  
enantio  
two ena  
metal at  
specific

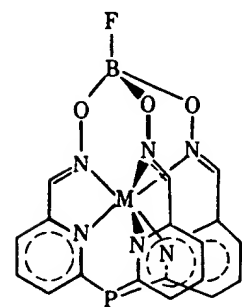
L. M. Ve

of which have the general formula  $M(L)_n$ . Finding them is a practical necessity.  $m$  and  $n$  are as defined in (2-XX).



that make them unusually interesting. Of high denticity they give very high coordination numbers. Of ion size that will best fit the cavity size, these ligands can be designed.

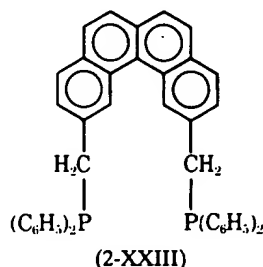
Synthesized apart from metal ions, other types of multicyclic ligand are synthesized around the metal ion and (2-XXII). An encapsulation under extremely acidic or basic conditions cannot be removed, can be oxidized to unusual coordination geometries; much closer to trigonal prismatic



(2-XXII)

bidentate ligands occupy cis positions. Two potential donor atoms separated by one atom span two trans positions would

have a very low probability of actually doing so. It would be more likely to form only one bond to a given metal atom, while using its second donor atom to coordinate to a different metal atom, or not at all. This is simply an inorganic example of the well-known problem in organic chemistry of synthesizing very large rings. By appropriately designing the connection between the donor atoms, however, ligands that span trans positions in a square complex or the two sites in a linear LML complex can be made. An example is (2-XXIII). Large chelate ring compounds<sup>7</sup> with 12 to 72 membered rings can be made from flexible bidentate ligands [e.g.,  $Me_2N(CH_2)_nNMe_2$  or  $R_2P(CH_2)_nPR_2$ ].



(2-XXIII)

## 2-6. Conformation of Chelate Rings

Simple diagrams of chelate rings in which the ring conformation is ignored are adequate for many purposes. Indeed, in some cases, such as  $\beta$ -diketonate complexes, the rings are planar and no problem arises. The relative stabilities and certain spectroscopic properties of many chelate complexes, however, can be understood only by considering carefully the effects of the ring conformations, as in the important case of five-membered rings such as those formed by ethylenediamine.

Figure 2-2 shows three ways of viewing the puckered rings, and identifies the absolute configurations in the  $\lambda, \delta$  notation. As indicated clearly in the figure, the chelate ring has as its only symmetry element a  $C_2$  axis. It must therefore (see Appendix 5) be chiral, and the two forms of a given ring are enantiomorphs. When this source of enantiomorphism is combined with the two enantiomorphous ways,  $\Lambda$  and  $\Delta$  of orienting the chelate rings about the metal atom (Fig. 2-3), a number of diastereomeric molecules become possible, specifically, the following eight:

$\Lambda(\delta\delta\delta)$	$\Delta(\lambda\lambda\lambda)$
$\Lambda(\delta\delta\lambda)$	$\Delta(\lambda\lambda\delta)$
$\Lambda(\delta\lambda\lambda)$	$\Delta(\lambda\delta\delta)$
$\Lambda(\lambda\lambda\lambda)$	$\Delta(\delta\delta\delta)$

<sup>7</sup>L. M. Venanzi *et al.*, *Helv. Chim. Acta*, 1984, 67, 65.

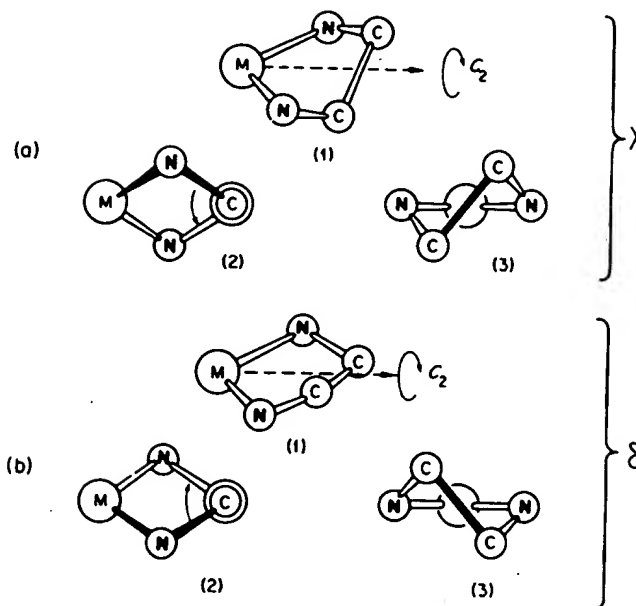


FIG. 2-2. Different ways of viewing the puckering of ethylenediamine chelate rings. The absolute configurations  $\lambda$  and  $\delta$  are defined. [Reproduced by permission from C. J. Hawkins; see General References.]

The two columns are here arranged so as to place an enantiomorphous pair on each line. In the following discussion we shall mention only members of the  $\Lambda$  series; analogous energy relationships must of course exist among corresponding members of the  $\Delta$  series.

The relative stabilities of the four diastereomers have been extensively investigated. First, it can easily be shown that the diastereomers must, in principle, differ in stability because there are different nonbonded (repulsive) interactions between the rings in each case. Figure 2-4 shows these differences for any two rings in the complex. When any reasonable potential function is used to estimate the magnitudes of the repulsive energies, it is concluded that

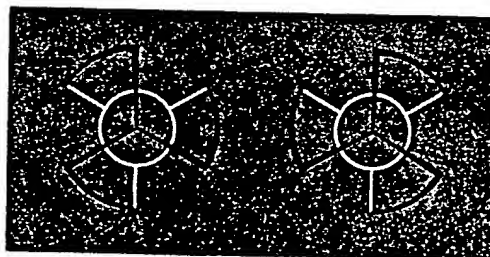
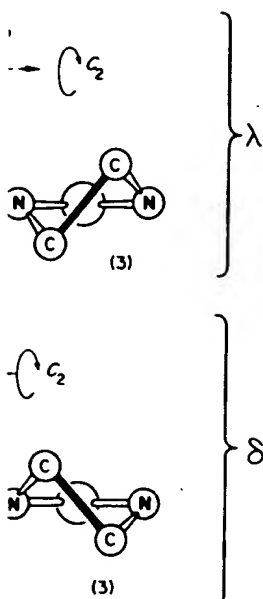


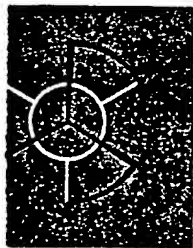
FIG. 2-3. Trischelate octahedral complexes (actual symmetry:  $D_3$ ) showing how the absolute configurations  $\Lambda$  and  $\Delta$  are defined according to the translation (twist) of the helices.



ethylenediamine chelate rings. The absolute configuration is determined by the direction of rotation (twist) of the helices. [Reproduced by permission from C. J. Hawkins; see General References.]

to place an enantiomorphous pair of diastereomers. We shall mention only members of the pair that must of course exist among corresponding diastereomers.

Diastereomers have been extensively studied, and it is concluded that the diastereomers must, in general, have different nonbonded (repulsive) interactions. Figure 2-4 shows these differences in terms of a reasonable potential function. By comparing the repulsive energies, it is concluded that



symmetry:  $D_3$ ) showing how the absolute configuration (twist) of the helices.

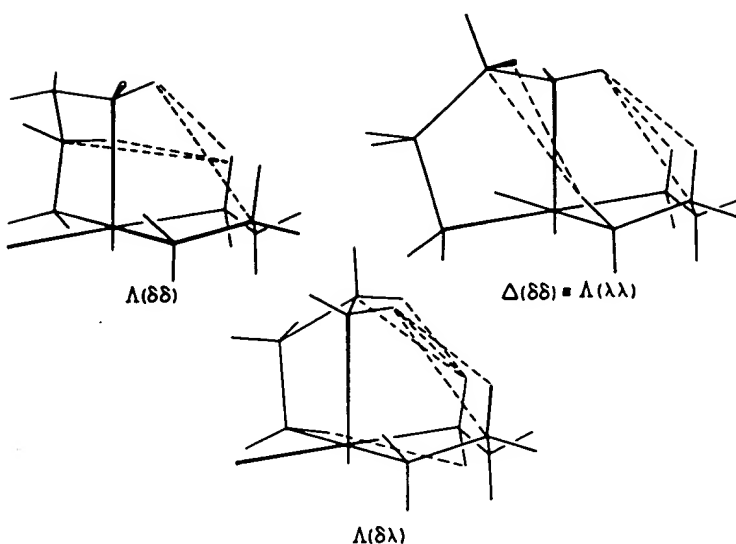


FIG. 2-4. The different sets of repulsive interactions that exist between the three different pairs of ring conformations in octahedral ethylenediamine complexes; broken lines represent the significant repulsive interactions. [Reproduced by permission from C. J. Hawkins; see General References.]

the order of decreasing stability is

$$\Lambda(\delta\delta\delta) > \Lambda(\delta\delta\lambda) > \Lambda(\delta\lambda\lambda) > \Lambda(\lambda\lambda\lambda)$$

This is not the actual order, however, because enthalpy differences between diastereomers are rather small ( $2-3 \text{ kJ mol}^{-1}$ ), and an entropy factor must also be considered. Entropy favors the  $\delta\delta\lambda$  and  $\delta\lambda\lambda$  species because they are three times as probable as the  $\delta\delta\delta$  and  $\lambda\lambda\lambda$  ones. Hence the best estimate of relative stabilities, which in fact agrees with all experimental data, becomes

$$\Lambda(\delta\delta\lambda) > \Lambda(\delta\delta\delta) \approx \Lambda(\delta\lambda\lambda) \gg \Lambda(\lambda\lambda\lambda)$$

In crystalline compounds, the  $\Delta(\delta\delta\delta)$  isomer (or its enantiomorph) has been found most often, but the other three have also been found. These crystallographic results probably prove nothing about the intrinsic relative stabilities, since hydrogen bonding and other intermolecular interactions can easily outweigh the small intrinsic energy differences.

Nuclear magnetic resonance studies of solutions of  $\text{Ru}^{II}$ ,  $\text{Pt}^{IV}$ ,  $\text{Ni}^{II}$ ,  $\text{Rh}^{III}$ ,  $\text{Ir}^{III}$ , and  $\text{Co}^{III}$   $[\text{M}(\text{en})_3]^{n+}$  complexes have yielded the most useful data, and the general conclusions seem to be that the order of stability suggested here is correct and that ring inversions are very rapid. Both experiment and theory suggest that the barrier to ring inversion is only  $\sim 25 \text{ kJ mol}^{-1}$ . Thus the four diastereomers of each overall form ( $\Lambda$  or  $\Delta$ ) are in labile equilibrium.

One of the interesting and important applications of the foregoing type of analysis is to the determination of absolute  $\Delta$  or  $\Lambda$  configurations by using

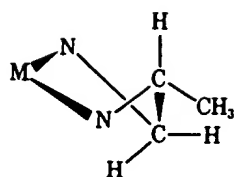


FIG. 2-5. The absolute configuration and expected conformation (i.e., with an equatorial  $\text{CH}_3$  group) for an  $\text{M}(\text{l-pn})$  chelate ring.

substituted ethylenediamine ligands of known absolute configuration. This is nicely illustrated by the  $[\text{Co}(\text{l-pn})_3]^{3+}$  isomers. The absolute configuration of  $\text{l-pn}$  [ $\text{pn} = 1,2\text{-diaminopropane}, \text{NH}_2\text{CH}(\text{CH}_3)\text{—CH}_2\text{NH}_2$ ] is known. It would also be expected from consideration of repulsions between rings in the tris complex (as indicated in Fig. 2-4) that  $\text{pn}$  chelate rings would always take a conformation that puts the  $\text{CH}_3$  group in an equatorial position. Hence, an  $\text{l-pn}$  ring can be confidently expected to have the  $\delta$  conformation shown in Fig. 2-5. Note that because of the extreme unfavorability of having axial  $\text{CH}_3$  groups, only two tris complexes are expected to occur, namely,  $\Lambda(\delta\delta\delta)$  and  $\Delta(\delta\delta\delta)$ . But by the arguments already advanced for  $\text{en}$  rings, the  $\Lambda$  isomer should be the more stable of these two, by 5 to 10  $\text{kJ mol}^{-1}$ . Thus we predict that the most stable  $[\text{Co}(\text{l-pn})_3]^{3+}$  isomer must have the absolute configuration  $\Lambda$  about the metal.

In fact, the most stable  $[\text{Co}(\text{l-pn})_3]^{3+}$  isomer is the one with  $+$  rotation at the sodium-D line, and it has the same circular dichroism spectrum, hence the same absolute configuration as  $(+)\text{[Co en}_3\text{]}^{3+}$ . The absolute configuration of the latter has been determined, and it is indeed  $\Lambda$ . Thus the argument based on conformational analysis is validated.

## 2-7. Second Sphere Coordination

The preceding discussion has dealt only with the ligands in direct contact with the metal ion—the *first coordination sphere* (FCS). Undoubtedly the next layer of molecules or ions—the *second coordination sphere* (SCS)—also displays a type of organization different from that in bulk solvent and dictated in part by its proximity to the metal ion and its FCS. In general, however, it is hard to establish any firm picture of the SCS, when it consists simply of a collection of solvent molecules. However, structured second coordination spheres formed by macrocyclic ligands can be often characterized in more detail, even by X-ray crystallography.

In many cases the major links between the two coordination spheres are hydrogen bonds between protic ligands ( $\text{NH}_3$ ,  $\text{en}$ , and  $\text{H}_2\text{O}$ ) in the FCS and the oxygen atoms of macrocyclic ethers that provide the SCS.<sup>8</sup> An example is provided by the “supercomplex” between  $(\text{COD})\text{Rh}(\text{NH}_3)_2$  and dibenzo-24-crown-8. Conversely, there may be hydrogen bonds between a surrounding

<sup>8</sup>H. M. Colquhoun *et al.*, *J. Chem. Soc. Dalton Trans.*, 1986, 1939; *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 487 (review).

protic  
bond  
woul  
and  
SCS  
duce

The  
ides,  
varic  
bipy  
tone  
comj  
or N  
to c  
[V p  
In  
nega  
can

<sup>9</sup>V. B  
<sup>10</sup>A. I



figuration and expected conformation group) for an  $M(l-pn)$  chelate ring.

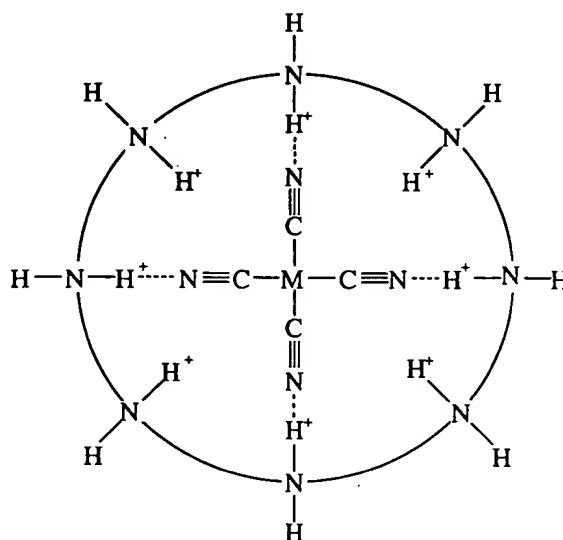
absolute configuration. This is The absolute configuration of  $[-CH_2NH_2]$  is known. It would sions between rings in the tris late rings would always take a equatorial position. Hence, an the  $\delta$  conformation shown in avorability of having axial  $CH_3$  to occur, namely,  $\Lambda(\delta\delta\delta)$  and ed for en rings, the  $\Lambda$  isomer  $10 \text{ kJ mol}^{-1}$ . Thus we predict ave the absolute configuration

is the one with + rotation at ar dichroism spectrum, hence  $[\alpha]^+$ . The absolute configuration ndeed  $\Lambda$ . Thus the argument

e ligands in direct contact with FCS). Undoubtedly the next ation sphere (SCS)—also dist in bulk solvent and dictated FCS. In general, however, it  $\delta$ , when it consists simply of a uctured second coordination : often characterized in more

two coordination spheres are en, and  $H_2O$ ) in the FCS and rovide the SCS.<sup>8</sup> An example (COD)Rh(NH<sub>3</sub>)<sub>2</sub> and dibenzo-bonds between a surrounding

protonated amine macrocycle and a central anionic complex,<sup>9</sup> as shown schematically in (2-XXIV). In both of these types of "supercomplex" the H-bonding forces are supplemented by other noncovalent interactions, and it would appear that in some cases, as illustrated by the complexes of (COD)PtCl<sub>2</sub> and [(COD)RhCl]<sub>2</sub> with cyclodextrins,<sup>10</sup> the forces between the FCS and the SCS are entirely of the secondary types, namely, dipole-dipole, dipole-induced dipole, van der Waals, and so on.



(2-XXIV)

### $\pi$ -ACID OR $\pi$ -BONDING LIGANDS: $\pi$ COMPLEXES

The ligands for which  $\pi$  bonding is important are carbon monoxide, isocyanides, substituted phosphines, arsines, stibines or sulfides, nitric oxide, and various molecules with delocalized  $\pi$  orbitals. These include pyridine, 2,2'-bipyridine, 1,10-phenanthroline, and certain ligands containing 1,2-dithioke-tone or 1,2-dithiolene groups, such as the dithiomaleonitrile anion. Diverse complexes exist, ranging from binary molecular compounds such as  $Cr(CO)_6$  or  $Ni(PF_3)_4$  through mixed species such as  $Co(CO)_3NO$  and  $(C_6H_5)_3PFe(CO)_4$ , to complex ions such as  $[Fe(CN)_5CO]^{3-}$ ,  $[Mo(CO)_5I]^-$ ,  $[Mn(CNR)_6]^+$ ,  $[V(phen)_3]^+$ , and  $[Ni(S_2C_2(CN)_2)_2]^{2-}$ .

In many of these complexes, the metal atoms are in low-positive, zero, or negative formal oxidation states. It is a characteristic of the ligands that they can stabilize low oxidation states. This property is associated with the fact

<sup>9</sup>V. Balzani et al., *J. Chem. Soc. Chem. Commun.*, 1984, 55.

<sup>10</sup>A. Harada and S. Takahashi, *J. Chem. Soc. Chem. Commun.*, 1986, 1229.

that in addition to lone pairs, these ligands possess *vacant  $\pi$  orbitals*. These vacant orbitals accept electron density from filled metal orbitals to form a type of  $\pi$  bonding that supplements the  $\sigma$  bonding arising from lone-pair donation; high electron density on the metal atom—of necessity in low oxidation states—thus can be delocalized onto the ligands. The ability of ligands to accept electron density into low-lying empty  $\pi$  orbitals can be called  $\pi$  *acidity*, the word “acidity” being used in the Lewis sense.

There are many unsaturated organic molecules and ions that are also capable of forming complexes with transition metals in low oxidation states, and these are called  $\pi$  *complexes*. There is a qualitative difference from  $\pi$ -acid ligands. The latter form bonds to the metal involving  $\sigma$  orbitals and  $\pi$  orbitals whose nodal planes include the axis of the  $\sigma$  bond. For the  $\pi$ -complexing ligands such as alkenes, arenes, and allyl groups, *both* the donation and back-acceptance (see next section) of electron density by the ligand are accomplished using ligand  $\pi$  orbitals. The metal is thus out of the molecular plane of the ligand, whereas with  $\pi$ -acid ligands the metal atom lies along the axes of the linear ligands or in the plane of planar ones.

In a third class of ligand that involves  $\pi$  bonding there are metal-oxygen or metal-nitrogen multiple bonds, as in  $\text{O}=\text{VCl}_3$ ,  $\text{MnO}_4^-$ , and  $\text{N}\equiv\text{OsO}_3^-$ . Here the electron flow is in the opposite sense to that in the bonding of  $\pi$ -acid ligands (i.e., from  $p$  orbitals on O or N to the metal  $d$  orbitals).

We now survey the main classes of ligands that form  $\pi$  bonds to metal atoms. The chemical properties of metal carbonyls and metal complexes with the other  $\pi$ -bonding ligands will be presented in Chapter 22 and in sections dealing with the chemistry of NO, phosphorus (III) compounds, and so on.

## 2-8. $\pi$ -Acid Ligands: CO as the Prototype

Ligands capable of accepting an appreciable amount of  $\pi$ -electron density, from the metal atoms into empty  $\pi$  or  $\pi^*$  orbitals of their own are referred to as  $\pi$ -acceptor or  $\pi$ -acid ligands. Of these, carbon monoxide is the most important and the most extensively studied. We shall discuss the principal way in which it forms bonds to metals, namely, in a linear  $\text{M}-\text{C}-\text{O}$  fashion in detail here. In Chapter 22, the chemistry of metal carbonyls as a class (including the other forms of bonding in which CO engages) will be discussed. In Section 2-9 the way in which some similar ligands (such as  $\text{RNC}$ ,  $\text{N}_2$ ,  $\text{NO}$ ) function as  $\pi$ -acid ligands will be compared with the behavior of CO.

The way in which CO (and many other  $\pi$ -acid ligands similarly) engages in bonding to a metal atom may be stated as follows:

1. Overlap of a filled carbon  $\sigma$  orbital with a  $\sigma$ -type orbital on the metal atom as in Fig. 2-6a. Electron flow  $\text{C} \rightarrow \text{M}$  in such a dative overlap would lead to an unacceptable concentration of electron density on the metal atom when the latter is not a +2 or more highly charged ion. The metal therefore attempts to reduce this charge (Pauling's electroneutrality principle) by push-

FIG.  
atom  
omit

ing  
has

2

the  
elec

7

refe

as a

at ti

mal

Thu

and

the

clos

7

rela

by r

mol

som

cert

in a

plex

7

mul

Acc

don

$\equiv$

by s

by s

by s

by s

by s

by s

possess vacant  $\pi$  orbitals. These filled metal orbitals to form a bonding arising from lone-pair atom—of necessity in low oxidation ligands. The ability of ligands to donate  $\pi$  orbitals can be called  $\pi$  Lewis sense.

molecules and ions that are also carbonyl metals in low oxidation states, the qualitative difference from  $\pi$ -metal involving  $\sigma$  orbitals and  $\pi$  orbitals of the  $\sigma$  bond. For the  $\pi$ -com-allyl groups, both the donation of electron density by the ligand and the metal atom lies along the axis of planar ones.

In bonding there are metal-oxygen complexes such as  $\text{VCl}_3$ ,  $\text{MnO}_4^-$ , and  $\text{N}\equiv\text{OsO}_3^-$ . In the bonding of  $\pi$ -metal to the metal  $d$  orbitals). In metal carbonyls and metal complexes with  $\pi$  ligands in Chapter 22 and in sections 22.3 (III) compounds, and so on.

amount of  $\pi$ -electron density, orbitals of their own are referred to as carbon monoxide is the most important. We shall discuss the principal features of a linear  $\text{M}-\text{C}-\text{O}$  fashion of metal carbonyls as a class of  $\text{CO}$  engages) will be discussed. Ligands (such as  $\text{RNC}$ ,  $\text{N}_2$ ,  $\text{NO}$ ) with the behavior of  $\text{CO}$ .

acid ligands similarly) engages as follows:

1. a  $\sigma$ -type orbital on the metal atom such a dative overlap would be formed from density on the metal atom and the ligand. The metal therefore obeys the electroneutrality principle) by push-

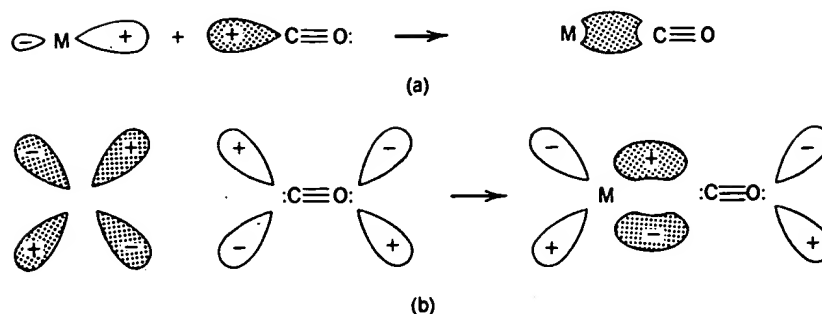


FIG. 2-6. (a) The formation of the metal  $\leftarrow$  carbon  $\sigma$  bond using an unshared pair on the C atom. (b) The formation of the metal  $\rightarrow$  carbon  $\pi$  bond. The other orbitals on the CO are omitted for clarity.

ing electrons back to the ligand. This of course is possible *only* if the ligand has suitable acceptor orbitals.

2. A second dative overlap of a filled  $d\pi$  or hybrid  $dp\pi$  metal orbital with the empty,  $p\pi$  orbital on carbon monoxide, which can act as a receptor of electron density (Fig. 2-6b).

This bonding mechanism is *synergic*, since the drift of metal electrons, referred to as "back-bonding", into CO orbitals, will tend to make the CO as a whole negative, hence to increase its basicity via the  $\sigma$  orbital of carbon; at the same time the drift of electrons to the metal in the  $\sigma$  bond tends to make the CO positive, thus enhancing the acceptor strength of the  $\pi$  orbitals. Thus up to a point the effects of  $\sigma$ -bond formation strengthen the  $\pi$  bonding, and vice versa. It may be noted here that dipole moment studies indicate that the moment of an  $\text{M}-\text{C}$  bond is only very low, about 0.5 D, suggesting a close approach to electroneutrality.

There have been many efforts to provide a detailed accounting of the relative importance of  $\sigma$  and  $\pi$  components of the bonding in metal carbonyls by means of molecular orbital calculations.<sup>11</sup> However, even for the simplest molecules, namely,  $\text{M}(\text{CO})_x$  ( $x = 4, 5, 6$ ), it is not feasible to avoid making some important approximations, whose final effects on the results are uncertain. Hence, it is probably wiser to rely primarily on experimental evidence in attempting to understand the bonding in metal carbonyls and related complexes of  $\pi$ -acid ligands.

Two important and broadly useful lines of physical evidence showing the multiple nature of  $\text{M}-\text{CO}$  bonds are bond lengths and vibrational spectra. According to the preceding description of the bonding, as the extent of back-donation from M to CO increases, the  $\text{M}-\text{C}$  bond becomes stronger and the  $\text{C}\equiv\text{O}$  bond becomes weaker. Thus, the multiple bonding should be evidenced by shorter  $\text{M}-\text{C}$  and longer  $\text{C}-\text{O}$  bonds as compared to  $\text{M}-\text{C}$  single bonds

<sup>11</sup>C. W. Bauschlicher, Jr., and P. S. Bagus, *J. Chem. Phys.*, 1984, **81**, 5889.

and  $\text{C}\equiv\text{O}$  triple bonds, respectively. Actually very little information can be obtained from the CO bond lengths, because in the range of bond orders (2–3) concerned, CO bond length is relatively insensitive to bond order. The bond length in CO itself is 1.128 Å, while the bond lengths in metal carbonyl molecules are  $\sim 1.15$  Å, a shift in the proper direction but of little quantitative significance owing to its small magnitude and the uncertainties ( $\sim 0.02$  Å) in the individual distances. For M—C distances, the sensitivity to bond order in the range concerned (1–2) is relatively high, probably  $\sim 0.3$  to  $0.4$  Å per unit of bond order, and good evidence for multiple bonding can therefore be expected from such data. To do this we measure the lengths of M—CO bonds in the same molecule in which some other bond, M—X exists, such that this bond must be single. Then, using the known covalent radius for X, estimating the single bond covalent radius of C to be  $0.70$  Å when an  $sp$  hybrid orbital is used (the greater  $s$  character makes this  $\sim 0.07$  Å shorter than that for  $sp^3$  carbon), the length for a single M—CO bond in this molecule can be estimated and compared with the observed value.

Figure 2-7 shows some substitution products of  $\text{Cr}(\text{CO})_6$  in which three or four CO groups have been replaced by ligands such as aliphatic amine nitrogen, which has no capacity to compete with CO trans to it for  $\pi$  bonding or  $\text{PH}_3$ , which has very little capacity to do so. We see that in such cases the remaining CO groups have even shorter Cr—C bonds because of even more extensive development of Cr—C  $\pi$ -back-bonding. The shortening is greater in (b) than in (c), since there is slight  $\pi$  bonding to the phosphorus atoms of  $\text{PH}_3$ . The shortening is also greater in (d) than in (c) because there are only two CO groups in (d) to compete for the available  $d\pi$  electrons of the chromium atom.

From the vibrational spectra of metal carbonyls, it is also possible to infer the existence and extent of M—C multiple bonding. This is most easily done by studying the CO stretching frequencies rather than the MC stretching frequencies, since the former give rise to strong sharp bands, well separated from all other vibrational modes of the molecules. The MC stretching frequencies, on the other hand, are in the same range with other types of vibration (e.g., MCO bends); therefore assignments are not easy to make, nor are the so-called MC stretching modes actually pure MC stretching motions. The inferring of M—C bond orders from the behavior of C—O vibra-

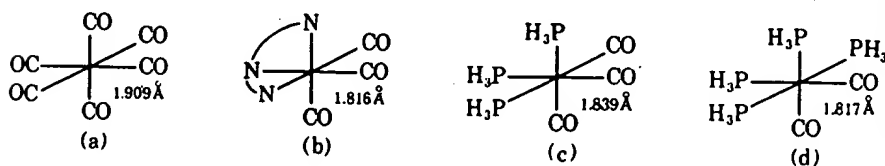


FIG. 2-7. Cr—C bond distances in (a)  $\text{Cr}(\text{CO})_6$ , (b)  $\text{fac}-[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2]\text{Cr}(\text{CO})_3$ , (c)  $\text{fac}-(\text{PH}_3)_3\text{Cr}(\text{CO})_3$ , and (d)  $\text{cis}-(\text{PH}_3)_2\text{Cr}(\text{CO})_4$ . [Data for (b) are from F. A. Cotton and D. C. Richardson, *Inorg. Chem.* 1966, 5, 1851. Data for (a), (c), and (d) are from G. Huttner and S. Schelle, *J. Crystallogr. Mol. Struct.*, 1971, 1, 69.]

tions  
given  
C—O  
freque

Fro  
ecules  
conclu  
2143 cm  
in the  
Moreo  
back-b  
some C  
ability  
to a gr  
metal  
cm<sup>-1</sup> (a  
are rep  
as Crd  
quenci  
the iso  
the me  
found  
illustra  
(cm<sup>-1</sup>)  
versely  
to CO  
the CO  
the foll

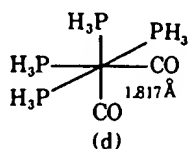
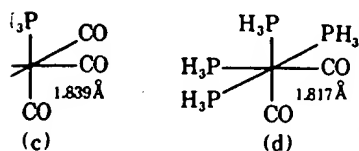
To o  
frequen  
of the C  
This pr  
The  
suasive,  
bonding  
Cr(CO)  
be respo  
the effe

J. L. Hu

very little information can be in the range of bond orders (2–insensitive to bond order. The bond lengths in metal carbonyl direction but of little quantitative the uncertainties ( $\sim 0.02$  Å) in s, the sensitivity to bond order h, probably  $\sim 0.3$  to  $0.4$  Å per multiple bonding can therefore be re the lengths of M—CO bonds and, M—X exists, such that this ovalent radius for X, estimating  $70$  Å when an  $sp$  hybrid orbital  $1.07$  Å shorter than that for  $sp^3$  in this molecule can be estimated

ts of  $\text{Cr}(\text{CO})_6$  in which three or s such as aliphatic amine nitro- CO trans to it for  $\pi$  bonding or We see that in such cases the C bonds because of even more ding. The shortening is greater ng to the phosphorus atoms of n in (c) because there are only lable  $d\pi$  electrons of the chro-

nyls, it is also possible to infer nding. This is most easily done ather than the MC stretching ng sharp bands, well separated cules. The MC stretching fre- ne range with other types of nments are not easy to make, ually pure MC stretching mo- n the behavior of C—O vibra-



ic- $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2]\text{Cr}(\text{CO})_3$ , a for (b) are from F. A. Cotton and (a), (c), and (d) are from G. Huttner

tions depends on the assumption that the valence of C is constant, so that a given increase in the M—C bond order must cause an equal decrease in the C—O bond order; this, in turn, will cause a drop in the CO vibrational frequency.

From the direct comparison of CO stretching frequencies in carbonyl molecules with the stretching frequency of CO itself, certain useful qualitative conclusions can be drawn. The CO molecule has a stretching frequency of  $2143\text{ cm}^{-1}$ . Terminal CO groups in neutral metal carbonyl molecules are found in the range  $2125$  to  $1850\text{ cm}^{-1}$ , showing the reduction in CO bond orders. Moreover, when changes are made that should increase the extent of M—C back-bonding, the CO frequencies are shifted to even lower values. Thus if some CO groups are replaced by ligands with low or negligible back-accepting ability, those CO groups that remain must accept  $d\pi$  electrons from the metal to a greater extent to prevent the accumulation of negative charge on the metal atom. Thus the frequencies for  $\text{Cr}(\text{CO})_6$  are  $\sim 2100$ ,  $2000$ , and  $1985\text{ cm}^{-1}$  (exact values vary with phase and solvent) whereas, when three CO's are replaced by amine groups that have essentially no ability to back-accept, as  $\text{Cr}(\text{dien})(\text{CO})_3$  (Fig. 2-7b), there are two CO stretching modes with frequencies of  $\sim 1900$  and  $1760\text{ cm}^{-1}$ . Similarly, when we go from  $\text{Cr}(\text{CO})_6$  to the isoelectronic  $\text{V}(\text{CO})_6^-$ , when more negative charge must be taken from the metal atom, a band is found at  $\sim 1860\text{ cm}^{-1}$  corresponding to the one found at  $\sim 2000\text{ cm}^{-1}$  in  $\text{Cr}(\text{CO})_6$ . A series of these isoelectronic species illustrating this trend, with their infrared-active CO stretching frequencies ( $\text{cm}^{-1}$ ) is  $\text{Ni}(\text{CO})_4$  ( $\sim 2060$ );  $\text{Co}(\text{CO})_4^-$  ( $\sim 1890$ );  $\text{Fe}(\text{CO})_4^{2-}$  ( $\sim 1790$ ). Conversely, a change that would tend to inhibit the shift of electrons from metal to CO  $\pi$  orbitals, such as placing a positive charge on the metal, should cause the CO frequencies to rise, and this effect has been observed in several cases, the following being representative:

$\text{Mn}(\text{CO})_6^+$ , $\sim 2090$	$\text{Mndien}(\text{CO})_3^+$ , $\sim 2020, \sim 1900$
$\text{Cr}(\text{CO})_6$ , $\sim 2000$	$\text{Crdien}(\text{CO})_3$ , $\sim 1900, \sim 1760$
$\text{V}(\text{CO})_6^-$ , $\sim 1860$	

To obtain semiquantitative estimates of M—C  $\pi$  bonding from vibrational frequencies, it is first necessary to carry out an approximate dynamical analysis of the CO stretching modes, thus to derive force constants for the CO groups. This procedure is discussed in Section 22-5.

The type of structural and spectroscopic evidence just noted, while persuasive, is nonetheless rather indirect. More direct evidence for M—CO  $\pi$  bonding has recently been obtained by photoelectron spectroscopy.<sup>12</sup> For  $\text{Cr}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  the photoionization of one of those electrons that must be responsible for whatever M—CO  $\pi$  bonding exists was carried out and the effect of removing such an electron on the frequency of the totally sym-

<sup>12</sup>J. L. Hubbard and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1982, 104, 2132.

metric M—C stretching vibration in the resulting  $M(CO)_6^+$  ion measured. The frequency of this vibration was, in each case, found to be significantly lower than that of the corresponding vibration in the neutral  $M(CO)_6$  molecule, that is, by 10% for  $W(CO)_6^+$  and 15% for  $Cr(CO)_6^+$ . This unequivocally shows that the orbitals from which the electrons have been removed contribute importantly to the M—C bond strengths. By a further analysis of these same data it was shown that the loss of one such electron causes increases of  $\sim 0.14$  and  $0.10$  Å in the Cr—C and W—C distances, respectively.

### 2-9. Other $\pi$ -Acid Ligands

We shall specifically mention here the following CO-like  $\pi$ -acid ligands: RNC,  $N_2$ , CS, NO, and NS. The first three are isoelectronic with CO, while NO and NS have one more electron. The chemistry of compounds that contain these ligands is discussed in later sections (RNC and CS in Chapter 8;  $N_2$ , NO, and NS in Chapter 10) and we are concerned here only with discussing their ability to serve as  $\pi$ -acid ligands and how, in each case, it compares with that of CO.

**Isocyanide Ligands.** (See Section 8-11 for chemistry.) Isocyanides are capable of displaying as great  $\pi$ -acceptor capacity as CO when linked to a metal center capable of strong  $\pi$  donation, and this may be described using the same pattern of orbital overlaps as previously discussed for M—CO bonding. Both spectroscopic evidence (lowering of C—N stretching frequencies) and structural evidence [short M—C distances, such as  $1.94$  Å in  $Cr(CNPh)_6$ ] demonstrate this. The important difference between CO and RNC is that the latter is not an *obligatory*  $\pi$  acid. That is, while CO is such a weak Lewis base that the stability of M—CO bonds requires the synergic participation of both  $\sigma$  donation and  $\pi$  acceptance, isocyanides are good Lewis bases and can form bonds to higher-valent metal ions where there is essentially only  $\sigma$  donation involved.

It may be noted here that the cyanide ion ( $CN^-$ ) is also isoelectronic with CO and RNC, but its capacity to serve as a  $\pi$  acid is much lower and from the point of view of bonding it is perhaps best regarded as a pseudohalide rather than as a  $\pi$ -acid ligand. See Section 8-10 for the chemistry of  $CN^-$ .

**Dinitrogen.** Although  $N_2$  is isoelectronic with CO and RNC, and isosteric with the former, it is far more inert and the first dinitrogen complex,  $[Ru(NH_3)_5(N_2)]^{2+}$  was discovered only in 1965. Dinitrogen can be bound to metal atoms only in the presence of other ligands; there are no homoleptic complexes analogous to those formed by CO or RNC.

The bonding in *linear* M—N—N groups is qualitatively similar to that in terminal M—CO groups; the same two basic components,  $M \leftarrow N_2$   $\sigma$  donation and  $M \rightarrow N_2$   $\pi$  acceptance, are involved. The major quantitative differences, which account for the lower stability of  $N_2$  complexes, appear to arise from small differences in the energies of the MO's of CO and  $N_2$ . For CO the  $\sigma$ -donor orbital is weakly antibonding, whereas the corresponding orbital for  $N_2$  is of bonding character. Thus  $N_2$  is a significantly poorer  $\sigma$  donor than is

resulting  $M(CO)_6^+$  ion measured. In this case, found to be significantly lower than in the neutral  $M(CO)_6$  molecule for  $Cr(CO)_6^+$ . This unequivocally shows that the π-back-bonding contributions have been removed contribute to a further analysis of these same complexes. The electron causes increases of  $\sim 0.14$  cm<sup>-1</sup>, respectively.

ing CO-like π-acid ligands: RNC, isoelectronic with CO, while NO is not. The chemistry of compounds that contain RNC and CS in Chapter 8;  $N_2$ , concerned here only with discussing how, in each case, it compares

for chemistry.) Isocyanides are less reactive as CO when linked to a metal and this may be described using the same language discussed for M—CO bonding (e.g., C—N stretching frequencies) as, such as 1.94 Å in  $Cr(CNPh)_6$ . The difference between CO and RNC is that the π-back-bonding while CO is such a weak Lewis base requires the synergic participation of the π-orbitals. The π-orbitals of isocyanides are good Lewis bases and where there is essentially only σ

$(CN^-)$  is also isoelectronic with CO. The π-acid is much lower and from this it is best regarded as a pseudohalide. The bond order is 10 for the chemistry of  $CN^-$ . The difference with CO and RNC, and isosteric with CO, is that the first dinitrogen complex,  $[Cr(N_2)_6]^{3+}$ , is known. Dinitrogen can be bound to transition metal complexes; there are no homoleptic complexes of RNC.

The bonding is qualitatively similar to that in the CO complexes,  $M \leftarrow N_2$  σ donation and π-back-bonding. The major quantitative differences, in the CO complexes, appear to arise from the difference of CO and  $N_2$ . For CO the σ-donation is the corresponding orbital for π-back-bonding is significantly poorer σ donor than is

CO. Now it is observed that in pairs of  $N_2$  and CO complexes where the metal and other ligands are identical, the fractional lowerings of  $N_2$  and CO frequencies are nearly identical. For the CO complexes, weakening of the CO bond, insofar as electronic factors are concerned, is due entirely to back-donation from metal  $d\pi$  orbitals to CO  $\pi^*$  orbitals, with the σ donation slightly canceling some of this effect. For  $N_2$  complexes, on the other hand,  $N \equiv N$  bond weakening results from both σ donation and π back-acceptance. The very similar changes in stretching frequencies for these two ligands suggest then that  $N_2$  is weaker than CO in both its σ-donor and π-acceptor functions. This in turn would account for the poor stability of  $N_2$  complexes in general. Terminal dinitrogen compounds have N—N stretching frequencies in the region 1930 to 2230 cm<sup>-1</sup> ( $N_2$  has  $\nu = 2331$  cm<sup>-1</sup>). For discussion of chemistry, see Section 10-9.

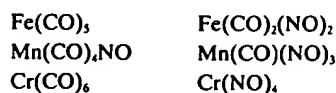
**The CS Ligand.** Although the CS molecule cannot be isolated, complexes containing the M—CS unit are known (cf. Section 8-13). The synergic σ/π interactions in M—CS units are similar to those in M—CO units, but perhaps somewhat stronger.

**The NO Ligand.** The NO molecule is closely akin to the CO molecule except that it contains one more electron, which resides in a  $\pi^*$  orbital. Loss of this electron gives  $NO^+$  which is isoelectronic with CO.

Just as the CO group reacts with a metal atom that presents an empty σ orbital and a pair of filled  $d\pi$  orbitals, as illustrated in Fig. 2-6, to give a linear MCO grouping with a C → M σ bond and a significant degree of M → C π bonding, so the NO group engages in a structurally and electronically analogous reaction with a metal atom that may be considered, at least formally, to present an empty σ orbital and a pair of  $d\pi$  orbitals containing only three electrons. The full set of four electrons for the  $Md\pi \rightarrow \pi^*(NO)$  interactions is thus made up of three electrons from M and one from NO. In effect, NO contributes three electrons to the total bonding configuration under circumstances where CO contributes only two. Thus for purposes of formal electron "bookkeeping," the ligand NO can be regarded as a three-electron donor in the same sense as the ligand CO is considered a two-electron donor. This leads to the following very useful general rules concerning stoichiometry, which may be applied without specifically allocating the difference in the number of electrons to any particular (i.e., σ or π) orbitals:

1. Compounds isoelectronic with one containing an  $M(CO)_n$  grouping are those containing  $M'(CO)_{n-1}(NO)$ ,  $M''(CO)_{n-2}(NO)_2$ , and so on, where  $M'$ ,  $M''$ , and so on, have atomic numbers that are 1, 2, . . . , and so on, < M. Some examples are  $(\eta-C_5H_5)CuCO$ ,  $(\eta-C_5H_5)NiNO$ ;  $Ni(CO)_4$ ,  $Co(CO)_3NO$ ,  $Fe(CO)_2(NO)_2$ ,  $Mn(CO)(NO)_3$ ;  $Fe(CO)_5$ ,  $Mn(CO)_4NO$ .

2. Three CO groups can be replaced by two NO groups. Examples of pairs of compounds so related are





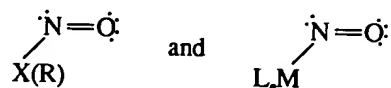
It may be noted that  $\text{Cr}(\text{NO})_4$  is the only known homoleptic metal nitrosyl complex. It is isoelectronic with  $\text{Ni}(\text{CO})_4$  and similarly has a tetrahedral structure, with a very short Cr—N distance (1.763 Å).<sup>13</sup> Claims for  $\text{Co}(\text{NO})_3$ ,  $\text{Fe}(\text{NO})_4$ , and  $\text{Ru}(\text{NO})_4$  have never been confirmed.

It should be noted that the designation "linear MNO group" does not disallow a small amount of bending in cases where the group is not in an axially symmetric environment, just as with terminal MCO groups. Thus MNO angles of 161 to 175° may be found in "linear" MNO groups. Truly "bent MNO groups" have angles of 120 to 140°.

In compounds containing both MCO and linear MNO groups, the M—C and M—N bond lengths differ by a fairly constant amount, ~0.07 Å, approximately equal to the expected difference in the C and N radii, and suggest that under comparable circumstances M—CO and M—NO bonds are typically about equally strong. In a chemical sense the M—N bonds appear to be stronger, since substitution reactions on mixed carbonyl nitrosyl compounds typically result in displacement of CO in preference to NO. For example,  $\text{Co}(\text{CO})_3\text{NO}$  reacts with a variety of  $\text{R}_3\text{P}$ ,  $\text{X}_3\text{P}$ , amine, and RNC compounds, invariably to yield the  $\text{Co}(\text{CO})_2(\text{NO})\text{L}$  product.

The NO vibration frequencies for linear MNO groups substantiate the idea of extensive M—N  $\pi$  bonding, leading to appreciable population of NO  $\pi^*$  orbitals. Both the NO and  $\text{O}_2^+$  species contain one  $\pi^*$  electron and their stretching frequencies are 1860 and 1876  $\text{cm}^{-1}$ , respectively. Thus the observed frequencies in the range 1800–1900  $\text{cm}^{-1}$ , which are typical of linear MNO groups in molecules with small or zero charge, indicate the presence of approximately one electron pair shared between metal  $d\pi$  and NO  $\pi^*$  orbitals.

Since nitrosyl halides (Section 10-8) and nitroso alkanes are bent, similar metal complexes can be anticipated:



A typical example is  $\text{IrCl}_2(\text{NO})(\text{PPh}_3)_2$  where the MNO angle is 123°. The NO here is best regarded as a 1e donor or as  $\text{NO}^-$ ;  $\pi$  bonding is not involved. Bridging NO groups, where NO can be regarded as a 3e donor, are also known.

These aspects and reactions of coordinated NO are discussed in more detail in Section 10-10.

The sulfur analogues with M—NS bonds are discussed in Section 10-10.

## 2-10. $\pi$ -Acid Ligands: Trivalent Phosphorus Compounds

Compounds of the type  $\text{PX}_3$  (as well as  $\text{AsX}_3$ ,  $\text{SbX}_3$ ,  $\text{SX}_2$ , and  $\text{SeX}_2$  species), especially when X is relatively electronegative, such as Ph, OR, Cl, or F, are important  $\pi$ -bonding ligands. This is particularly true of  $\text{PF}_3$  which forms

<sup>13</sup>K. Hedberg *et al.*, *Inorg. Chem.*, 1985, 24, 2776.

<sup>14</sup>J. F. Nixon, *Adv. Inorg. Chem. Radiochem.*, 1985, 29, 42.

many c  
Cr(PF<sub>3</sub>  
Lewis l  
little o  
transiti  
states.  
distanc  
discuss

In a  
replace  
or Bu)  
detail  
Mo(CC  
and ste  
structu

Whil  
edged f  
widely  
cificall  
it has b  
phosph  
accepti  
phorus  
lacking  
38 kJ n

FIG. 2-8.  
the PX<sub>3</sub> li  
the xy pla

<sup>15</sup>B. E. Bu  
<sup>16</sup>F. W. B.  
<sup>17</sup>F. A. Co  
<sup>18</sup>W. C. Ti  
1984, 106,  
M. Braga,  
<sup>19</sup>G. Huni

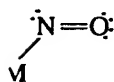


own homoleptic metal nitrosyl complex similarly has a tetrahedral structure (1.83 Å).<sup>13</sup> Claims for Co(NO)<sub>3</sub>, bridged.

"linear MNO group" does not exist where the group is not in an end-on terminal MCO groups. Thus "linear" MNO groups. Truly 0°.

In linear MNO groups, the M—C bond is constant amount, ~0.07 Å, ap- proximately the C and N radii, and suggest that the M—NO bonds are typi- cally the M—N bonds appear to be mixed carbonyl nitrosyl com- plexes in preference to NO. For R<sub>3</sub>P, X<sub>3</sub>P, amine, and RNC (NO)L product.

O groups substantiate the idea of appreciable population of NO π\* in one π\* electron and their orbitals respectively. Thus the observed bond lengths are typical of linear MNO complexes, indicate the presence of ap- proximately metal dπ and NO π\* orbitals. Nitrosyl alkanes are bent, similar



the MNO angle is 123°. The M—N bond; π bonding is not involved. Nitrosyl complexes, regarded as a 3e donor, are also

O are discussed in more detail

discussed in Section 10-10.

### Compounds

for bX<sub>3</sub>, SX<sub>2</sub>, and SeX<sub>2</sub> species), such as Ph, OR, Cl, or F, are generally true of PF<sub>3</sub> which forms

many compounds comparable to those of CO,<sup>14</sup> for example, Ni(PF<sub>3</sub>)<sub>4</sub> and Cr(PF<sub>3</sub>)<sub>6</sub>. Tertiary phosphines and phosphites, however, are also much better Lewis bases than CO and can form many complexes where π acidity plays little or no role. This is observed with the phosphine complexes of the early transition metals and with metal atoms of any kind in their higher oxidation states. In compounds such as NbBr<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>3</sub> or PtCl<sub>4</sub>(PMePh<sub>2</sub>)<sub>2</sub> the M—P distances show no evidence of significant π bonding. Phosphorus ligands are discussed in Section 11-18.

In almost any CO-containing molecule, one or more CO groups can be replaced by a PX<sub>3</sub> or similar ligand. The ability of PR<sub>3</sub> ligands (R = Me, Et, or Bu) to compete with CO groups for metal dπ electrons can be studied in detail by photoelectron spectroscopy<sup>15</sup> and vibrational spectroscopy in Mo(CO)<sub>n</sub>(PR<sub>3</sub>)<sub>6-n</sub> species and similar ones. The significant σ-donor ability<sup>16</sup> and steric requirements<sup>17</sup> of such ligands is also important in regard to the structures of M(CO)<sub>x</sub>(PR<sub>3</sub>)<sub>y</sub> type molecules.

While the occurrence of M → P dative π bonding is a generally acknowledged fact, the explanation for it entails controversy. The classical, and still widely credited, picture is that shown in Fig. 2-8, in which phosphorus specifically employs a pair of its d orbitals to accept metal electrons. However, it has been proposed, on the basis of quantum mechanical calculations that phosphorus p orbitals and the P—X σ\* orbitals may play a major role in accepting metal dπ electrons, even to the complete exclusion of the phosphorus dπ orbitals.<sup>18a</sup> Experimental evidence for or against such ideas is lacking. Rotation about the M—P bond with relatively small barriers (32–38 kJ mol<sup>-1</sup>) can be shown by nmr methods.<sup>18b</sup>

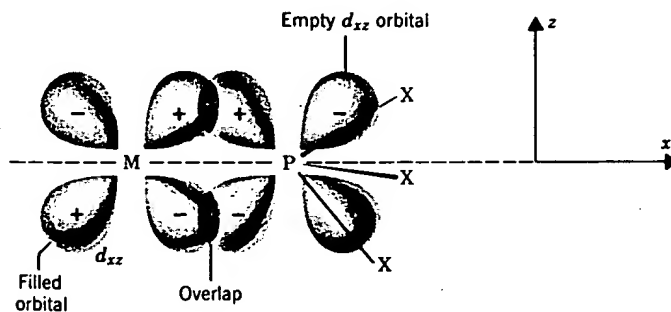


FIG. 2-8. The back-bonding from a filled metal *d* orbital to an empty phosphorus *3d* orbital in the PX<sub>3</sub> ligand taking the internuclear axis as the *x* axis. An exactly similar overlap occurs in the *xy* plane using the *d<sub>xy</sub>* orbitals.

<sup>14</sup>B. E. Bursten *et al.*, *Inorg. Chem.*, 1984, 23, 4361.

<sup>15</sup>F. W. B. Einstein *et al.*, *Inorg. Chem.*, 1985, 24, 2777.

<sup>16</sup>F. A. Cotton *et al.*, *Inorg. Chem.*, 1982, 21, 294.

<sup>17</sup>W. C. Troglor *et al.*, *J. Am. Chem. Soc.*, 1983, 105, 7033; D. S. Marynick, *J. Am. Chem. Soc.*, 1984, 106, 4064; A. G. Orpen and N. G. Connelly, *J. Chem. Soc. Chem. Commun.*, 1985, 1310; M. Braga, *Inorg. Chem.*, 1985, 24, 2702.

<sup>18</sup>G. Hunter *et al.*, *J. Chem. Soc. Dalton Trans.*, 1987, 1545.

Of course, the Lewis basicities of the  $PX_3$  ligands vary considerably,<sup>19</sup> and not entirely predictably<sup>20</sup> with X. This must be taken into consideration because, as with other classes of ligands, the synergistic relationship between  $\sigma$  donation and  $\pi$  acceptance (regardless of the exact mechanism for the latter) is also a source of ambiguity in understanding this class of ligands.<sup>21</sup>

The extent of both donation from the lone pair on the P atom and back-donation depends on the nature of the groups attached to P. For  $PH_3$  and  $P(\text{alkyl})_3$ ,  $\pi$ -acceptor ability is very low, but it becomes important with more electronegative groups. Analogous  $PX_3$ ,  $AsX_3$ , and  $SbX_3$  compounds differ very little, but the ligands having a nitrogen atom, which lacks  $\pi$  orbitals, cause significantly lower frequencies for the CO vibrations, as indicated by the CO stretching frequencies ( $\text{cm}^{-1}$ ) in the following series of compounds:

$(PCl_3)_3Mo(CO)_3$	2040, 1991
$(AsCl_3)_3Mo(CO)_3$	2031, 1992
$(SbCl_3)_3Mo(CO)_3$	2045, 1991
dien $Mo(CO)_3$	1898, 1758

The pronounced effect of the electronegativity of the groups X is shown by the following CO stretching frequencies

$[(C_6H_5)_3P]_3Mo(CO)_3$	1937, 1841
$[(C_6H_5O)_3P]_3Mo(CO)_3$	1994, 1922
$[Cl_2(C_6H_5O)P]_3Mo(CO)_3$	2027, 1969
$(Cl_3P)_3Mo(CO)_3$	2040, 1991
$(F_3P)_3Mo(CO)_3$	2090, 2055

The most electronegative substituent, F in  $PF_3$ , will reduce very substantially the  $\sigma$ -donor character so that there will be less  $P \rightarrow M$  electron transfer, and  $Md\pi \rightarrow Pd\pi$  transfer should be aided. The result is that  $PF_3$  and CO are quite comparable in their  $\pi$ -bonding capacity.

Attempts to order a large number of  $PX_3$ ,  $AsX_3$ , and  $SbX_3$  ligands according to their net  $\pi$ -accepting capacity have been made using  $LNi(CO)_3$  compounds, and to a lesser extent others such as  $LCr(CO)_3$ . Both the CO stretching frequencies and the  $^{13}C$  chemical shifts of the CO groups have been used as the indicative experimental parameter<sup>22</sup> and the two orderings are in general agreement. Based on these data some of the more common phosphorus li-

<sup>19</sup>T. T. Derencsengi *Inorg. Chem.*, 1981, 20, 665.

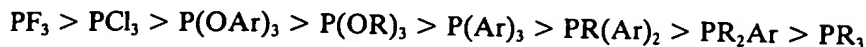
<sup>20</sup>G. M. Bancroft *et al.*, *Inorg. Chem.*, 1986, 25, 3675.

<sup>21</sup>W. P. Giering *et al.*, *Organometallics*, 1985, 4, 1981; see also R. V. Honeychuck and W. H. Hersch, *Inorg. Chem.*, 1987, 26, 1826.

<sup>22</sup>G. M. Bodner *et al.*, *Inorg. Chem.*, 1980, 19, 1951; T. Bartik *et al.*, *J. Organomet. Chem.*, 1984, 272, 29.

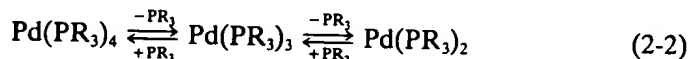
gands vary considerably,<sup>19</sup> and taken into consideration be-  
ergistic relationship between  $\sigma$   
exact mechanism for the latter)  
this class of ligands.<sup>21</sup>  
pair on the P atom and back-  
attached to P. For  $\text{PH}_3$  and  
becomes important with more  
, and  $\text{SbX}_3$  compounds differ  
atom, which lacks  $\pi$  orbitals,  
O vibrations, as indicated by  
following series of compounds:

gands come out in the following order (As and Sb ligands come very close to the corresponding P ligands):



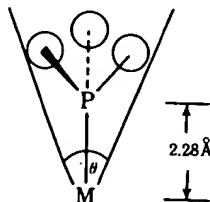
There is also structural evidence to support this general order.<sup>23</sup> For example, in  $(\text{PhO})_3\text{PCr(CO)}_5$  the P—Cr bond is 0.11 Å shorter than that in  $\text{Ph}_3\text{PCr(CO)}_5$ .

Of at least as great importance to the chemistry of  $\text{PX}_3$  compounds as the electronic factors are *steric factors*.<sup>24</sup> Indeed these may be more important or even dominant in determining the stereochemistries and structures of compounds. Steric factors also affect rates and equilibria of dissociation reactions such as eq. 2-2 and the propensity of phosphine complexes to undergo oxidative-addition reactions, or form olefin complexes.<sup>25</sup>



The stereochemistry of phosphine ligands is the prime factor in many highly selective catalytic reactions of phosphine complexes, such as hydroformylation and asymmetric hydrogenation (Chapter 28).

The steric requirement of a  $\text{PX}_3$  ligand is usually expressed by Tolman's cone angle,  $\theta$ , as defined below. The cone in question is one that can just enclose the van der Waals surface of all ligand atoms over all rotational orientations about the M—P bond.\* Triphenylphosphine has  $\theta = 145^\circ$  and  $\text{P(OCH}_3)_3$  has  $\theta = 107 \pm 2^\circ$ . It might have been expected that compounds with smaller cone angles would be better ligands, but since such compounds



are stronger bases, it is not always easy to distinguish steric from electronic factors although some progress in this respect is being made<sup>24</sup>. However, increasing the cone angle by having bulky groups tends to favor (a) lower coordination numbers, (b) the formation of less sterically crowded isomers, and (c) increased rates and equilibria in dissociative reactions. An example

<sup>23</sup>J. L. Atwood *et al.*, *Organometallics*, 1985, 4, 867.

<sup>24</sup>C. A. Tolman, *Chem. Rev.*, 1977, 77, 313; see also W. P. Giering *et al.*, *Organometallics*, 1987, 6, 650 for discussion of steric and  $\sigma$  and  $\pi$  electronic effects and their separation.

<sup>25</sup>C. A. Tolman *et al.*, *Organometallics*, 1983, 2, 1391.

\*More sophisticated definitions have been suggested but offer little practical advantage. See, for example, T. Bartik *et al.*, *J. Organomet. Chem.*, 1984, 272, 29.

1991  
1992  
1991  
1758

ty of the groups X is shown

37, 1841  
94, 1922  
27, 1969  
40, 1991  
90, 2055

ill reduce very substantially  
→ M electron transfer, and  
ult is that  $\text{PF}_3$  and CO are

, and  $\text{SbX}_3$  ligands according  
using  $\text{LNi(CO)}_3$  compounds,  
5. Both the CO stretching  
groups have been used as  
two orderings are in general  
re common phosphorus li-

so R. V. Honeychuck and W. H.

rtik *et al.*, *J. Organomet. Chem.*,

of the latter effect is provided by the reactions



where  $K$  varies from  $>1$  for  $\text{L} = \text{PPh}_3$  ( $\theta = 145^\circ$ ) to  $<10^{-10}$  for  $\text{L} = \text{P(OEt)}_3$  ( $\theta = 109^\circ$ ).

### 2-11. Multiple Bonds from Ligands to Metals

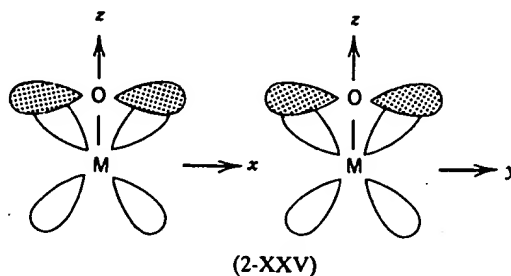
The concept of metal-ligand bonds as simple two-electron  $\text{L} \rightarrow \text{M}$  donor bonds has broad applicability. As noted in Sections 2-8 through 2-10 a significant amount of  $\text{M} \rightarrow \text{L}$   $\pi$  bonding must be superimposed upon this for  $\text{M}-\text{CO}$ ,  $\text{M}-\text{NO}$ , and other related ligands. Thus, these metal-ligand bonds have partial  $\pi$  character and bond orders  $>1$  (but  $<1.5$ ). However, there are many cases in which metal atoms form full double and triple bonds, either to nonmetal atoms (ligands) or to other metal atoms. The various multiple metal-metal bonds are discussed in Chapter 23.

We are concerned here with bonds of the types<sup>26</sup>



as well as some  $\text{M}-\text{X}-\text{M}$  systems where multiple bond character is present in the  $\text{M}-\text{X}-\text{M}$  bonds. In all of these cases, overlap between ligand atom  $p\pi$  orbitals and metal atom  $d\pi$  orbitals must be invoked to account for bonding in addition to the  $\text{M}-\text{X}$   $\sigma$  bonds.

**$\text{M}=\text{O}$  and  $\text{M}=\text{O}-\text{M}$  Bonds.** The  $\text{M}=\text{O}$  bonds are extremely numerous. In general, the distances are very short, namely, 1.5 to 1.8 Å depending on oxidation numbers, other ligands, and so on. In many cases the bond order is probably significantly  $>2$  because there are two filled  $p\pi$  orbitals on the oxygen atom, both of which can engage in bonding to appropriately directed  $d\pi$  orbitals on the metal atom, as shown in (2-XXV). There is no reason why, in many cases, that both of these interactions cannot proceed to the point where the sum of the two partial dative  $\pi$  bonds exceeds the bonding that would be provided by just one such interaction at its full extent. Thus, when a double bond,  $\text{M}=\text{O}$  is written, this should be regarded as a formalism and not an accurate specification of bond order.



<sup>26</sup>W. A. Herrmann, *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 56.

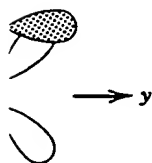
ns  
L  
45°) to  $<10^{-10}$  for  $L = P(OEt)_3$

ils  
le two-electron  $L \rightarrow M$  donor  
sections 2-8 through 2-10 a sig-  
be superimposed upon this for  
Thus, these metal-ligand bonds  
(but  $<1.5$ ). However, there are  
double and triple bonds, either  
al atoms. The various multiple  
types<sup>26</sup>

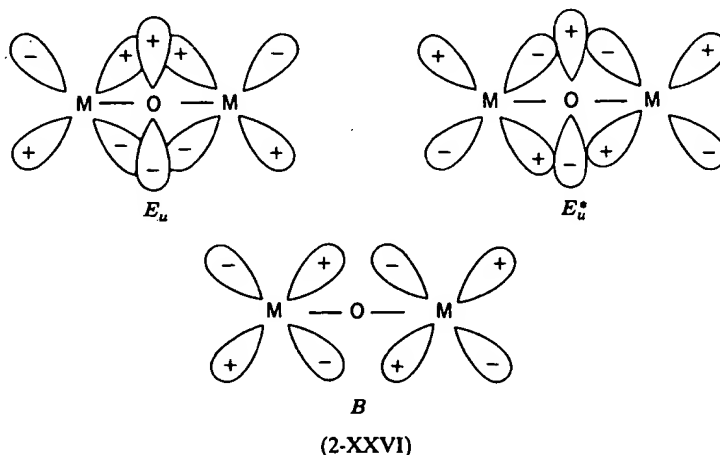


Multiple bond character is present  
, overlap between ligand atom  
invoked to account for bonding

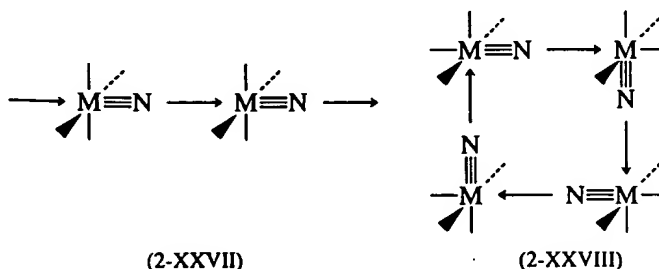
O bonds are extremely numer-  
ically, 1.5 to 1.8 Å depending  
1. In many cases the bond order  
e two filled  $p\pi$  orbitals on the  
nding to appropriately directed  
(2-XXV). There is no reason  
actions cannot proceed to the  
:  $\pi$  bonds exceeds the bonding  
reaction at its full extent. Thus,  
ould be regarded as a formalism  
er.



There are also many examples of linear  $M-O-M$  units, and in these more delocalized  $\pi$  bonding occurs. The  $[Cl_2MOMCl_2]^{n-}$  ions provide straightforward examples.<sup>27</sup> It may be assumed that by using a pair of  $sp$  hybrid orbitals on the oxygen atom a linear pair of  $M-O-M$   $\sigma$  bonds is formed. There are then two orthogonal, occupied  $p\pi$  orbitals on the oxygen atom that can interact with suitable metal  $d\pi$  orbitals. Now, however, there is a total of four such  $d\pi$  orbitals and two sets of  $\pi$  interactions (2-XXVI) (one in the  $xz$  plane and the other just like it in the  $yz$  plane) will be established. With both of the two components of the  $E_u$  orbital occupied, there is a total of four  $\sigma$  electrons and four  $\pi$  electrons, and thus each  $M-O$  bond may be assigned (formally) a bond order of 2. This is consistent with the occurrence of  $M-O$  distances in the range of 1.75 to 1.90 Å for various  $M-O-M$  systems.<sup>27</sup>



**Metal-Nitrogen Multiple Bonds.**<sup>28</sup> As with oxygen there are two types,  $M \equiv N$  and  $M=N=M$ , but the former show a pronounced tendency towards association, either into linear chains (2-XXVII) or cycles (2-XXVIII) as found in  $MoNCl_3$ . For discussion of chemistry, see Section 10-18.

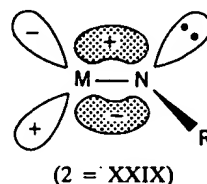


<sup>27</sup>F. A. Cotton and R. C. Najar, *Inorg. Chem.*, 1981, 20, 1866.

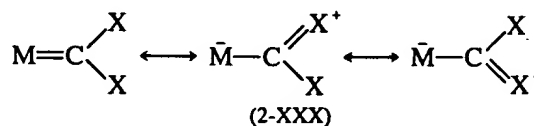
<sup>28</sup>R. Hoffmann *et al.*, *J. Am. Chem. Soc.*, 1986, 108, 5381.

The types of orbital overlaps entailed in the formation of  $M\equiv N$  and  $M=N=M$  bonds are entirely analogous to those already discussed for the oxo cases. As full triple bonds, the  $M\equiv N$  linkages are generally very short (e.g., 1.66 Å in  $MoCl_4N^-$ , and 1.58 Å in  $ReCl_4N$ ), but the bonds in  $M=N=M$  systems are longer (~1.85 Å).

Metal to nitrogen double bonds<sup>29</sup> are found in the  $M=NR$  compounds, sometimes called nitrenes (by analogy to carbenes), but better designated metal imides. Here the bonding can be described in very conventional terms with one  $\sigma$  bond, one  $\pi$  bond and a lone pair of electrons, as in (2-XXIX).



**$M=CR_2$  and  $M\equiv CR$  bonds.** These play an enormous role in organometallic chemistry and will be discussed at length in Chapter 25. The nature of the M to C bonding is very much dependent on the nature of M and R.<sup>30</sup> At one extreme there are compounds in which M is in a high valence state and the R group(s) not of  $\pi$ -donor character. In these cases, the bonds are comparable to those just discussed for  $M=NR$  and  $M\equiv N$ . For these types of compounds, the terms *alkylidene* ( $M=CR_2$ ) and *alkylidyne* ( $M\equiv CR$ ) have been favored. On the other hand, when the metal is in a low valence state and the substituents on carbon are  $\pi$  donors, the M—C bonds are *not* full double or triple bonds and the systems are rendered stable by the migration of charge from the substituents (such as OR or NR) on the carbon atom, as shown in resonance terms in (2-XXX). In these types of compounds it is customary to use the terms *carbene complex* and *carbyne complex*. The chemistry is qualitatively different for the two classes of each type (i.e.,  $MCR_2$  and  $MCR$ ) of compound, as will be discussed in Chapter 25.



**Heavier Ligand Atoms.** We have just discussed the formation of M—X multiple bonds for the principal cases where X is an element from the first short period, namely, C, N, or O. It is to be noted that recently analogues for some of these, in which the heavier elements, Si, Ge, P, As, S, and Se occur, have been prepared, and doubtless this development will continue rapidly. As a first approximation the M—X bonding to the heavier X atoms

<sup>29</sup>W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, 31, 123.

<sup>30</sup>E. A. Carter and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1986, 108, 4746.

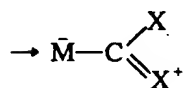
ation of  $M \equiv N$  and  $M=N=M$  discussed for the oxo cases. As usually very short (e.g., 1.66 Å bonds) in  $M=N=M$  systems

and in the  $M=NR$  compounds, (benes), but better designated as in very conventional terms of electrons, as in (2-XXIX).

R

an enormous role in organometallic chemistry in Chapter 25. The nature of the bond between M and R.<sup>30</sup> When M is in a high valence state

In these cases, the bonds are between R and  $M \equiv N$ . For these types and *alkylidyne* ( $M \equiv CR$ ) have the metal in a low valence state. The  $M-C$  bonds are *not* fully considered stable by the migration of R to NR on the carbon atom, as in these types of compounds it is called a *carbyne complex*. The chemistry of each type (i.e.,  $MCR_2$  and Chapter 25.



discussed the formation of  $M-X$  where X is an element from the first row of the periodic table. It is noted that recently analogues of  $M \equiv N$ , Si, Ge, P, As, S, and Se are being developed which will continue to lead to the heavier X atoms

can be described in the same ways as for the light X atoms, but it is possible that outer *d* orbitals may make some contribution for the heavier X atoms. The greater size of the heavier elements may also be important in some cases. Whatever the reasons, compounds such as linear  $(C_5Me_5)(CO)_2 Mn=Ge=Mn(CO)_2(C_5Me_5)$  and bent  $(C_5Me_5)(CO)_2 Mn=Te=Mn(CO)_2(C_5Me_5)$  have no C or O analogues;  $M=C=M$  bonds are found in some porphyrin complexes however (Section 8-9).

Another type of linkage formed only by the heavier elements is displayed by the compounds  $Cp(CO)_2CrXCr(CO)_2Cp$ , where  $X = S, Se$  but not O. The very short bonds (e.g., 2.20 Å for Cr-Se), together with other considerations, have been taken to imply that  $Cr \equiv X$  triple bonds exist.

## π COMPLEXES OF UNSATURATED ORGANIC MOLECULES

Molecules that have multiple bonds ( $C=C$ ,  $C \equiv C$ ,  $C=O$ ,  $C=N$ ,  $S=O$ ,  $N=O$ , etc.) can form what are called *π complexes* with transition metals. The chemistry of these is discussed in detail in Chapter 26.

### 2-12. Alkenes and Alkynes

The most important *π* complexes are those of compounds with  $C=C$  bonds. The earliest known organotransition metal complex was discovered by W. C. Zeise in Copenhagen in about 1827, but the true constitution was not recognized until the 1950s. Zeise's salt,  $K[Pt(C_2H_4)Cl_3]$ , has ethylene bound to Pt as shown in Fig. 2-9a.

The key point is that the  $C=C$  axis of the coordinated alkene is perpendicular to one of the expected bond directions from the metal. The expected line of a bond orbital from the metal strikes the  $C=C$  bond at its midpoint (though for unsymmetrical alkenes, this need *not* be so).

Figure 2-9 shows several other examples of olefin complexes as well as a comparable dioxygen complex.

The most generally useful description of this type of bonding was developed for copper-alkene complexes by M. J. S. Dewar and later extended to other transition metals. Figure 2-10 illustrates the assumption that as with other *π*-bonding ligands like CO, there are *two* components to the total bonding: (a) overlap of the *π*-electron density of the olefin with a *σ*-type acceptor orbital on the metal atom and (b) a "back-bond" resulting from flow of electron density from filled metal *d<sub>xy</sub>* or other *dπ-pπ* hybrid orbitals into *antibonding* orbitals on the carbon atoms. This view is thus similar to that discussed for the bonding of carbon monoxide and similar weakly basic ligands and implies the retention of appreciable "double-bond" character in the olefin. Of course, the donation of *π*-bonding electrons to the metal *σ* orbital and the introduction of electrons into the *π*-antibonding orbital both weaken the *π* bonding in the

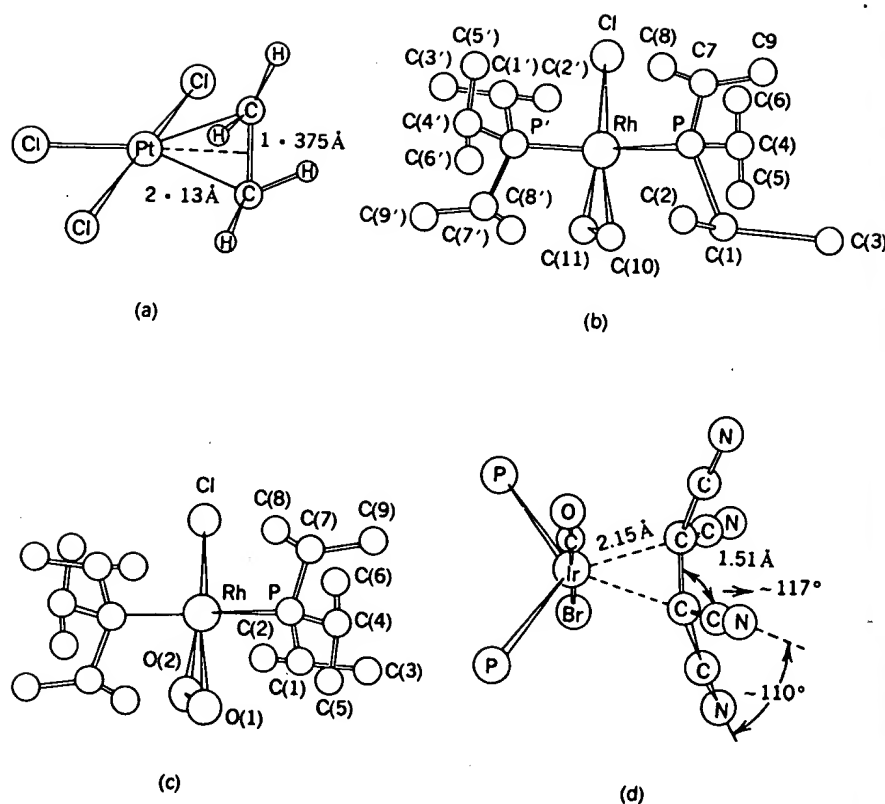


FIG. 2-9. (a) The structure of the ion in Zeise's salt. (b,c) The structures of ethylene and oxygen complexes, *trans*-RhCl(PPR<sub>3</sub>)<sub>2</sub>. (d) The structure of the tetracyanoethylene complex IrBr(CO)((CN)<sub>2</sub>C=C(CN)<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>.

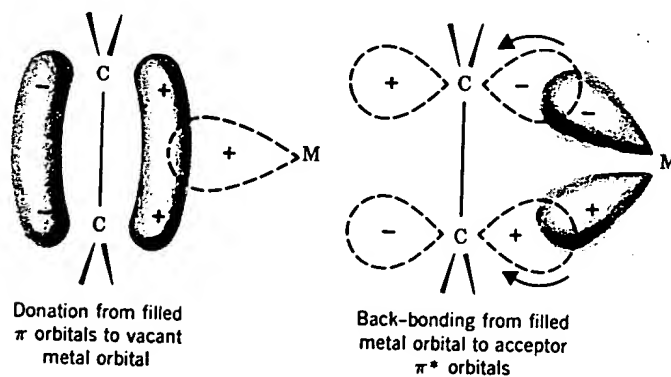


FIG. 2-10. The molecular orbital view of alkene-metal bonding according to Dewar.

olefin.  
length

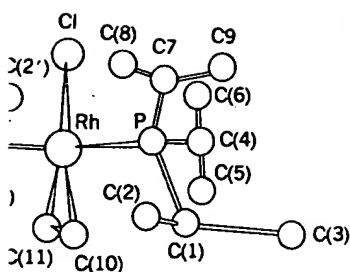
The  
ing ha  
the C-  
donati  
into th  
compe  
to pro  
ground  
with d

Alth  
the pla  
plexes  
There  
olefin  
the pe  
basis (a  
In any  
an axis  
have g  
in-plan

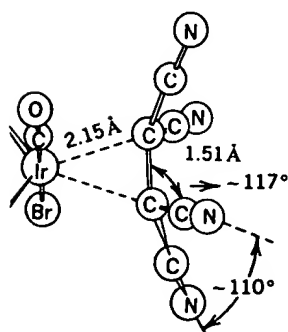
In c  
C—C  
the C<sub>2</sub>(  
approa  
bonding  
(2-XX)  
molecu  
fashion  
XXXIe

S. Miya  
N. Kasa  
6, 1211



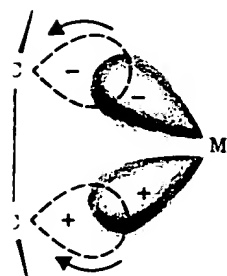


(b)



(d)

the structures of ethylene and oxygen  
the tetracyanoethylene complex



ing from filled  
d to acceptor  
orbitals

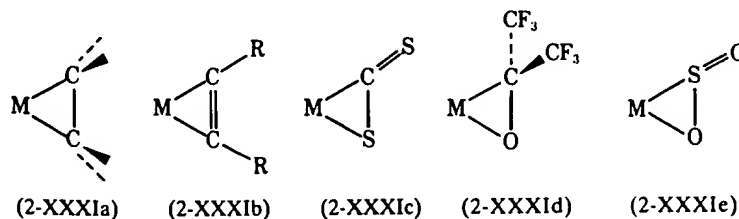
bonding according to Dewar.

olefin, and in every case except the anion of Zeise's salt there is significant lengthening of the olefin C—C bond.

The important qualitative idea about metal-olefin bonding is that the bonding has dual character. There is donation of those electrons initially forming the C—C  $\pi$  bond into a metal orbital of suitable symmetry, and there is donation of electrons from filled metal orbitals of suitable symmetry back into the  $\pi$ -antibonding orbitals of the olefin. As in the CO case, the two components are synergically related. As one component increases, it tends to promote an increase in the other. On both theoretical and experimental grounds, it appears that the metal-alkene bond is essentially electroneutral, with donation and back-acceptance approximately balanced.

Although, as we have seen, the C—C axis of ethylene is perpendicular to the plane of the square coordination for Zeise's salt and other, similar complexes [Fig. 2-9(a) and (b)], this is not strongly demanded by the bonding. There is also a metal  $d\pi$  orbital *in the plane*, and it too can interact with the olefin  $p\pi^*$  orbital as shown in Fig. 2-10; the difference in stability between the perpendicular and in-plane orientations is thus not great on a bonding basis (although in-plane bonding is weaker) and may be mainly steric in origin. In any event, measurements of the barrier to rotation<sup>31</sup> of the olefin about an axis defined by a line from the metal atom to the midpoint of the olefin have given results of only 40–70 kJ mol<sup>-1</sup> and there is one case where the in-plane orientation is found<sup>32</sup>.

In complexes containing tetracyanoethylene (Fig. 2-9d) or F<sub>2</sub>C=CF<sub>2</sub> the C—C bond is about as long as a normal single bond and the angles within the C<sub>2</sub>(CN)<sub>4</sub> or C<sub>2</sub>F<sub>4</sub> ligand suggest that the carbon atoms bound to the metal approach tetrahedral hybridization. Indeed, it is possible to formulate the bonding as involving two normal 2c-2e metal-carbon bonds in a metallacycle (2-XXXIa) with approximately  $sp^3$  hybridized carbon. A number of other molecules that have multiple bonds and can be bound to metals in the  $\eta^2$  fashion can be regarded as forming metallacycles (2-XXXIb) through (2-XXXIe).



<sup>31</sup>S. Miya and K. Saito, *Inorg. Chem.*, 1981, 20, 287.

<sup>32</sup>N. Kasai *et al.*, *J. Am. Chem. Soc.*, 1983, 105, 2482; M. F. Rettig *et al.*, *Organometallics*, 1987, 6, 1211.

Actually, the metallacycle view and the  $\pi$ -donor view are neither incompatible nor mutually exclusive but are complementary, with a smooth gradation of one description into the other. The one to be preferred in any given case depends on the extent to which the double bond of the ligand has been reduced to a single bond. From a formal point of view, however, the metallacycle view entails a problem with oxidation state. For example, a compound such as  $\text{Ni}(\text{C}_2\text{F}_4)(\text{CO})_3$  could be regarded as a nickel(II) rather than a nickel(0) complex. Clearly, in a compound such as  $\text{Pt}(\text{C}_2\text{H}_4)_3$ , it would be absurd to propose  $\text{Pt}^{\text{VI}}$ . It is best to regard molecules bound sideways as neutral ligands that do not alter the formal oxidation state.

**Conjugated Alkenes.** When two or more conjugated double bonds are engaged in bonding to a metal atom the interactions become more complex, though qualitatively the two types of basic, synergic components are involved. The case of the 1,3-butadiene unit is an important one and shows why it would be a drastic oversimplification to treat such cases as simply collections of separate monoolefin-metal interactions.

Two extreme formal representations of the bonding of 1,3-butadiene to a metal atom are possible (Fig. 2-11). The structure (b) would imply that bonds 1-2 and 3-4 should be longer than bond 2-3. In  $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$  the bond lengths are approximately the same and  $^{13}\text{C}$ -H coupling constants in the nmr spectra indicate that the hybridization at carbon still approximates to  $sp^2$ . However, in some other compounds of conjugated cyclic alkenes, the pattern is of the long-short-long type, indicating some contribution from this extreme structure.

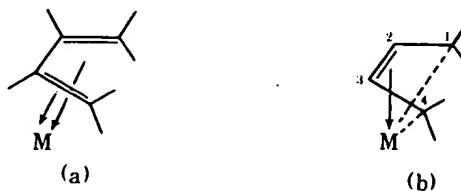


FIG. 2-11. Two extreme formal representations of the bonding of a 1,3-butadiene group to a metal atom: (a) implies that there are two more or less independent monoolefin metal interactions; (b) depicts  $\sigma$  bonds to C-1 and C-4 coupled with a monoolefin metal interaction to C-2 and C-3.

**Alkynes.** The presence of two mutually perpendicular  $\pi$  bonds in an alkyne makes for considerably more varied and complicated ligand behavior than that shown by alkenes. There is, of course, the simple use of one  $\pi$  bond and the associated  $\pi^*$  orbital in exactly the same way as found in olefin complexes. This results in a lengthening of the C—C distance and a marked deviation from linearity. Typical results are shown schematically in Fig. 2-12(a).

An alkyne can also behave as a formal four-electron donor to one metal atom. In addition to the type of interaction just discussed, the other pair of  $\pi$  electrons may be partially donated to a metal  $d\pi$  orbital lying perpendicular

FIG. 2-  
three, :

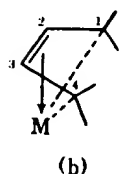
to the

donati  
those  
greate  
mensic  
electr

$\pi$ -donor view are neither incomplementary, with a smooth grade one to be preferred in any given double bond of the ligand has been point of view, however, the metal-  
n state. For example, a compound a nickel(II) rather than a nickel(0)  $\text{Pt}(\text{C}_2\text{H}_4)_3$ , it would be absurd to bound sideways as neutral ligands

ore conjugated double bonds are eractions become more complex, synergic components are involved. important one and shows why it at such cases as simply collections

he bonding of 1,3-butadiene to a icture (b) would imply that bonds 2-3. In  $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$  the bond C—H coupling constants in the at carbon still approximates to of conjugated cyclic alkenes, the ating some contribution from this



onding of a 1,3-butadiene group to a ss independent monoolefin metal inter- with a monoolefin metal interaction to C-

y perpendicular  $\pi$  bonds in an and complicated ligand behavior se, the simple use of one  $\pi$  bond e same way as found in olefin ie C—C distance and a marked e shown schematically in Fig.

ur-electron donor to one metal just discussed, the other pair of al  $d\pi$  orbital lying perpendicular

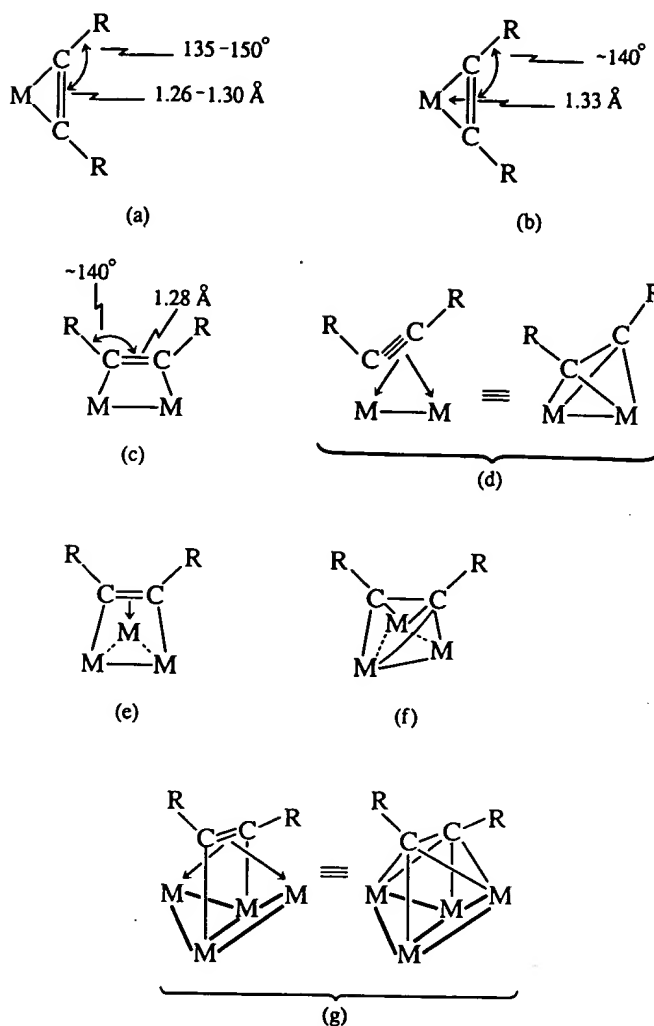


FIG. 2-12. Important modes of ligation of alkynes to single metal atoms and clusters of two, three, and four metal atoms.

to the plane of the three-membered  $\text{M}-\text{C}-\text{C}$  ring. Again, a synergistic back-

donation may also occur if there is a filled  $d$  orbital perpendicular to *both* of those already used. This is shown in Fig. 2-13. This typically leads to even greater lengthening of the C—C distance. Figure 2-12(b) shows typical dimensions and indicates how an additional arrow is used to represent this four-electron bonding.

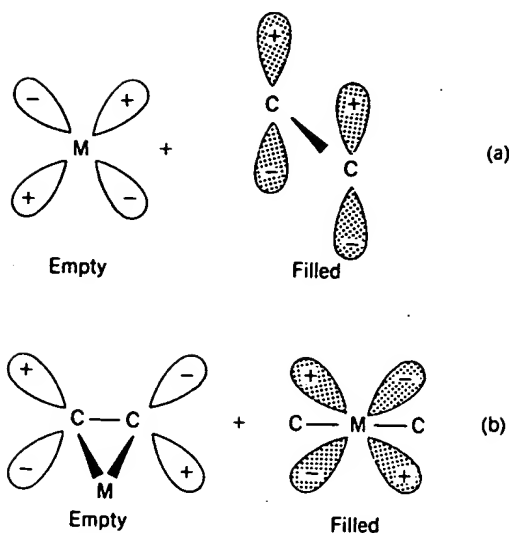


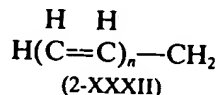
FIG. 2-13. The orbitals employed in the second synergic alkyne-to-metal bond.

When acting as a ligand toward two or more metal atoms, alkynes have a large repertoire of roles. With respect to a dimetal unit, there are two major types of structures, both describable as  $\eta^2, \mu_2$ ; they are shown in Fig. 2-12(c) and (d). In the planar structure of Fig. 2-12(c), the alkyne is a two-electron donor. In structure (d), which is a distorted tetrahedral shape, the alkyne is a four-electron donor. The bonding in Fig. 2-12(d) can be envisioned as donation of one pair of  $\pi$  electrons to each metal atom (with appropriate back-donation) or as the formation of two single bonds to each metal atom. The latter view is certainly too extreme since the C—C distances in these cases are in the range 1.30 to 1.35 Å.

With trinuclear sets of metal atoms there are again two principal geometries, Fig. 2-12(e) and (f), in each of which the alkyne is a formal four-electron donor. Finally, we note that towards a tetranuclear set of metal atoms, the geometry shown in Fig. 2-12(g), where the metal atoms have the nonplanar "butterfly" arrangement is common. Here, again, the alkyne is a formal four-electron donor.

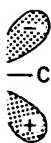
### 2-13. Enyl Ligands

Groups of the formal type 2-XXXII can interact with a metal atom so as to serve as  $(2n + 1)$ -electron ligands. The two cases of greatest interest are the allyl and pentadienyl groups.



(a)

(b)



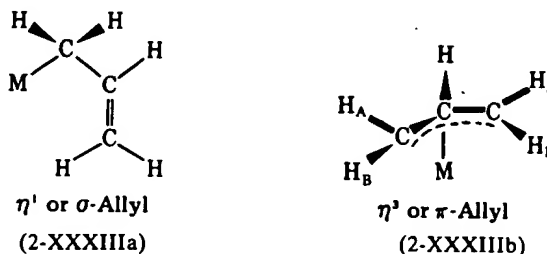
ergic alkyne-to-metal bond.

metal atoms, alkynes have a formal unit, there are two major types are shown in Fig. 2-12(c) the alkyne, is a two-electron donor. In a tetrahedral shape, the alkyne is shown in 2(d) can be envisioned as a four-electron donor to each metal atom (with appropriate bonds to each metal atom. The C—C distances in these

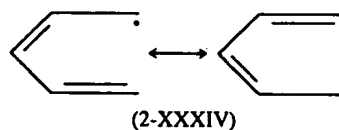
again two principal geometries. In the first, the alkyne is a formal four-electron donor to a pair of metal atoms, the alkyne is a formal four-

with a metal atom so as to form a complex of greatest interest are the

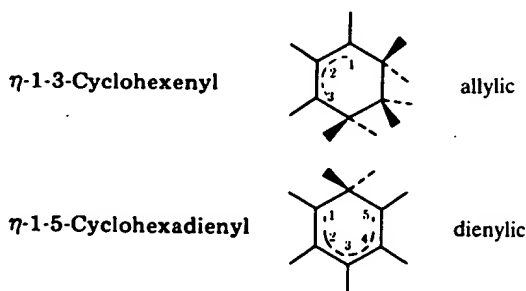
The allyl system displays both  $\eta^1$  (also often denoted  $\sigma$  behavior) (2-XXXIIIa) and  $\eta^3$  behavior, (2-XXXIIIb). Note that (1) the  $\eta^3$ -allyl group is a three-electron donor, and (2) the hydrogen atoms of the methylene groups are not equivalent. There are *syn*-( $H_A$ ) and *anti*-( $H_B$ ) protons that can be distinguished by nmr. Many allyls show nonrigid behavior in solution (Section 29-15).



The  $\eta^5$ -pentadienyl ligand<sup>33</sup>, as a five-electron donor in its semicircular, delocalised form represented schematically in 2-XXXIV is capable of forming a variety of metal complexes, including a so-called "open" ferrocene, ( $C_5H_5$ )<sub>2</sub>Fe.



It may also be noted that  $\eta^3$ -allyl and  $\eta^5$ -pentadienyl units are often found within rings, especially six-membered rings, namely,



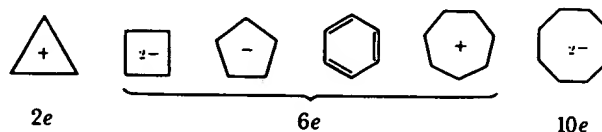
## 2-14. Aromatic Ring Systems

Just as the  $\pi$  electrons of alkenes can interact with metal  $d$  orbitals, so can certain of the delocalized  $\pi$ -electron ring systems of aromatic molecules overlap with  $d_{xz}$  and  $d_{yz}$  metal orbitals.

The first example of this type of complex was the molecule  $Fe(C_5H_5)_2$ , now

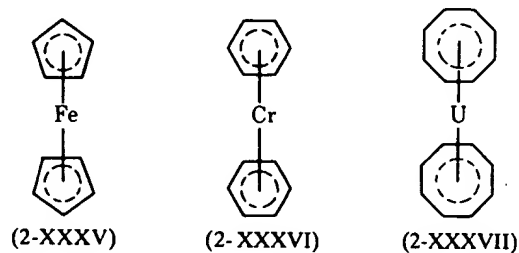
<sup>33</sup>R. D. Ernst, *Struct. Bonding (Berlin)*, 1984, **57**, 1-53.

known as *ferrocene*, in which the  $6\pi$ -electron system of the ion  $C_5H_5^-$  is bound to the metal. Other aromatic systems with the "magic numbers" of 2, 6, and 10 for the aromatic electronic configuration are the carbocycles:



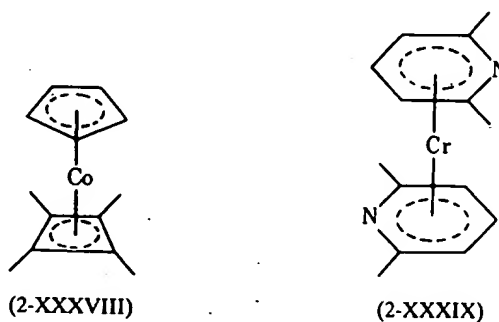
The  $C_5H_5$ ,  $C_6H_6$ , and  $C_8H_8$  rings are the most common in complexes, but the  $C_7H_7$  and  $C_4H_4$  systems also occur frequently. It should also be noted that for purposes of electron counting the ring system and the metal atom may be considered as neutral. For example, the total of 18 electrons in ferrocene can be regarded as 5 per  $C_5H_5$  ring plus 8 from Fe.

Compounds are known that have only  $\pi$ -bonded rings such as ferrocene (2-XXXV), dibenzenechromium (2-XXXVI), or  $(C_8H_8)_2U$  (2-XXXVII), but

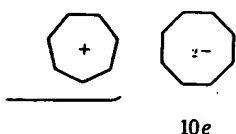


there are many compounds with one ring and other ligands such as halogens, CO, RNC, and  $R_3P$ . Examples are  $\eta-C_5H_5Mn(CO)_3$  and  $\eta-C_5H_5Fe(CO)_2Cl$ . The symbol  $\eta$  is used to signify that all carbon atoms of the ring are bonded to the metal atom. There are also molecules in which two different types of arene ring are present, such that the total number of  $\pi$  electrons they provide, plus those possessed by the metal atom itself, add to 18. For example, in (2-XXXVIII), there are five  $\pi$  electrons from  $C_5H_5$ , four from  $C_4R_4$ , and nine from Co. Similarly, we have  $(\eta-C_5H_5)(\eta-C_6H_6)Mn$ .

It is also possible for heterocyclic arene rings to form complexes, examples being  $(\eta-C_4H_4N)Mn(CO)_3$ ,  $(\eta-C_4H_4S)Cr(CO)_3$ ,  $(\eta-C_5H_5)(\eta-C_4H_4N)Fe$ ,  $(\eta-C_5H_5)(\eta-C_4H_4P)Fe$ , and (2-XXXIX).

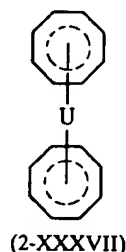


system of the ion  $C_5H_5^-$  is bound "magic numbers" of 2, 6, and 10 for the carbocycles:



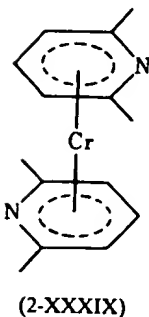
common in complexes, but the . It should also be noted that system and the metal atom may total of 18 electrons in ferrocene n Fe.

conded rings such as ferrocene or  $(C_8H_8)_2U$  (2-XXXVII), but



other ligands such as halogens,  $(CO)_3$  and  $\eta-C_5H_5Fe(CO)_2Cl$ . atoms of the ring are bonded in which two different types of er of  $\pi$  electrons they provide, add to 18. For example, in  $(2-H_5)$ , four from  $C_4R_4$ , and nine Mn.

gs to form complexes, exam-  $(CO)_3$ ,  $(\eta-C_5H_5)(\eta-C_4H_4N)Fe$ ,



The basic qualitative features of the bonding in ferrocene are well understood, and will serve to illustrate the basic principles for all  $(\eta-C_nH_n)_2M$  bonding, although for  $(C_8H_8)_2M$  systems there are a few additional points that are covered later.

The discussion of bonding does not depend critically on whether the preferred rotational orientation of the rings (see Fig. 2-14) in an  $(\eta-C_5H_5)_2M$  compound is staggered ( $D_{5d}$ ) or eclipsed ( $D_{5h}$ ); nor is that question unequivocally settled. It is experimentally certain that in ferrocenes the barrier to rotation is only about 8 to 20 kJ mol<sup>-1</sup>\*. The eclipsed configuration may be the more stable, but in condensed phases, especially crystals, where there are intermolecular energies of the same or greater magnitude than the barrier, either configuration may be found.

The bonding is best treated in the linear combination of atomic orbitals (LCAO-MO) approximation. A semiquantitative energy level diagram is given in Fig. 2-15. Each  $C_5H_5$  ring, taken as a regular pentagon, has five  $\pi$  MO's, one strongly bonding ( $a$ ), a degenerate pair that are weakly bonding ( $e_1$ ), and a degenerate pair that are markedly antibonding ( $e_2$ ), as shown in Fig. 2-16. The pair of rings taken together then has ten  $\pi$  orbitals and, if  $D_{5d}$  symmetry is assumed, so that there is a center of symmetry in the  $(\eta-C_5H_5)_2M$  molecule, there will be centrosymmetric ( $g$ ) and antisymmetric ( $u$ ) combinations. This is the origin of the set of orbitals shown on the left of Fig. 2-15. On the right are the valence shell ( $3d$ ,  $4s$ ,  $4p$ ) orbitals of the iron atom. In the center are the MO's formed when the ring  $\pi$  orbitals and the valence orbitals of the iron atom interact.

For  $(\eta-C_5H_5)_2Fe$ , there are 18 valence electrons to be accommodated: 5  $\pi$ -electrons from each  $C_5H_5$  ring and 8 valence shell electrons from the iron atom. It will be seen that the pattern of MO's is such that there are exactly 9 bonding or nonbonding MO's and 10 antibonding ones. Hence the 18 electrons can just fill the bonding and nonbonding MO's, giving a closed configuration. Since the occupied orbitals are either of  $a$  type (which are each symmetric around the 5-fold molecular axis) or they are *pairs* of  $e_1$  or  $e_2$  type, which are also, *in pairs*, symmetrical about the axis, no intrinsic barrier to

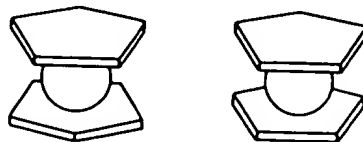


FIG. 2-14. Staggered and eclipsed configurations of an  $(\eta-C_5H_5)_2M$  compound. In crystalline ferrocene there are molecules of different orientations randomly distributed throughout the crystal (P. Seiler and J. D. Dunitz, *Acta Cryst.*, 1979, B35, 1068). Also, the H atoms of the rings are bent towards the metal (F. Takasagawa and J. F. Koetzle, *Acta Cryst.*, 1979, B35, 1074).

\*There are similar values for the rotation of rings in arene compounds; see J. Howard *et al.*, *J. Chem. Soc. Dalton Trans.*, 1982, 967, 977.

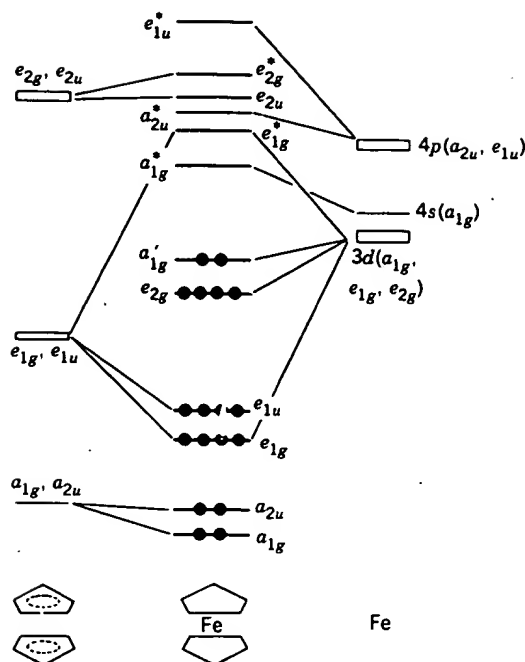


FIG. 2-15. An approximate MO diagram for ferrocene. Different workers often disagree about the exact order of the MO's; the order shown here, especially for the antibonding MO's, may be incorrect in detail, but the general pattern is widely accepted.

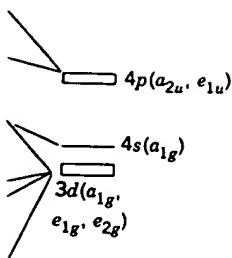
internal rotation is predicted. The very low barriers observed may be attributed to van der Waals forces directly between the rings.

Figure 2-15 indicates that among the principal bonding interactions is that giving rise to the strongly bonding  $e_{1g}$  and strongly antibonding  $e_{1g}^*$  orbitals. To give one concrete example of how ring and metal orbitals overlap, the nature of this particular important interaction is illustrated in Fig. 2-17. This particular interaction is in general the most important single one because the directional properties of the  $e_1$ -type  $d$  orbitals ( $d_{xz}$ ,  $d_{yz}$ ) give an excellent overlap with the  $e_1$ -type ring  $\pi$  orbitals, as Fig. 2-17 shows.

Systems containing only one  $\eta\text{-C}_5\text{H}_5$  ring include  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ ,  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ,  $(\eta\text{-C}_5\text{H}_5)\text{NiNO}$ , and  $(\eta\text{-C}_5\text{H}_5)\text{CuPR}_3$ . The ring-to-metal bonding in these cases can be accounted for by a conceptually simple modification of the picture given previously for  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  systems. In each case a principal axis of symmetry can be chosen so as to pass through the metal atom and intersect the ring plane perpendicularly at the ring center; in other words, the  $\text{C}_5\text{H}_5\text{M}$  group is a pentagonal pyramid, symmetry  $C_{5v}$ . The single ring may then be considered to interact with the various metal orbitals in about the same way as do each of the rings in the sandwich system. The only difference is that opposite to this single ring is a different set of ligands which



# INCIPLES



Fe

ie. Different workers often disagree about especially for the antibonding MO's, may ly accepted.

barriers observed may be attrib- en the rings.

incipal bonding interactions is that strongly antibonding  $e_{1g}^*$  orbitals. and metal orbitals overlap, the on is illustrated in Fig. 2-17. This important single one because the itals ( $d_{xz}$ ,  $d_{yz}$ ) give an excellent Fig. 2-17 shows.

g include  $(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ ,  $(\eta\text{-})\text{CuPR}_3$ . The ring-to-metal bond- conceptually simple modification 4 systems. In each case a principal ass through the metal atom and the ring center; in other words, , symmetry  $C_{5v}$ . The single ring : various metal orbitals in about the sandwich system. The only is a different set of ligands which

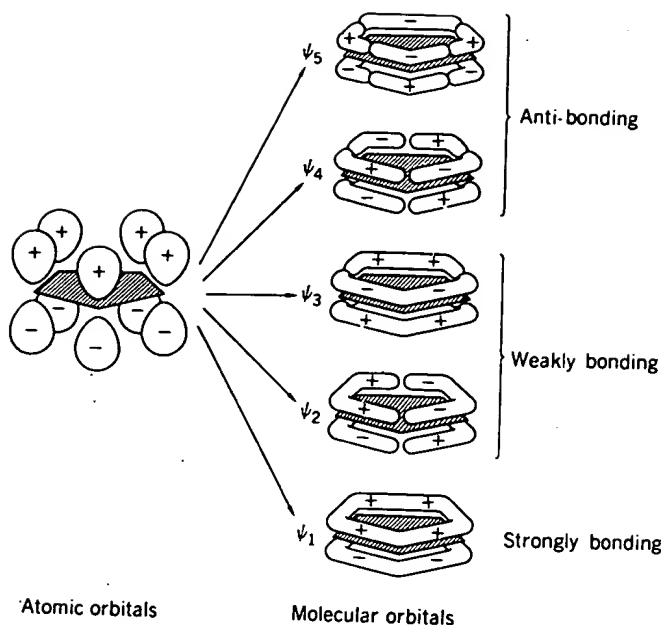


FIG. 2.16. The  $\pi$  molecular orbitals formed from the set of  $p\pi$  orbitals of the  $\text{C}_5\text{H}_5$  ring.

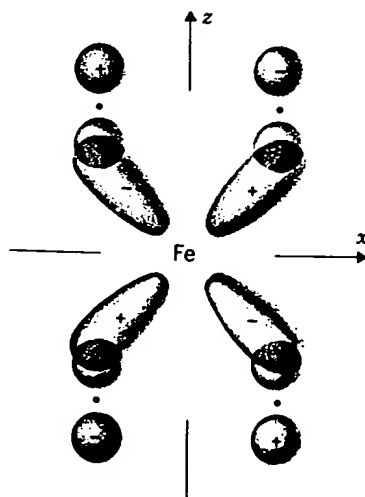


FIG. 2.17. Overlapping of one of the  $e_g$ -type  $d$  orbitals  $d_{xz}$  with an  $e_g$ -type  $\pi$  orbital to give a delocalized metal-ring bond: cross-sectional view taken in the  $xz$  plane.

interact with the opposite lobes of, for example, the  $de_1$  orbitals, to form their own appropriate bonds to the metal atom.

The MO picture of ring-to-metal bonding just given for ferrocene is *qualitatively* but *not quantitatively* applicable to other  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds, and with obvious modifications, to other  $(\eta\text{-arene})_2\text{M}$  molecules. Relative orbital energies can and do change as the metal is changed. Ferrocene itself has been treated by very elaborate MO calculations, and at the other extreme a ligand field model has also been applied to the  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds generally. Although it is clearly unrealistic to treat the bonding in these systems as electrostatic (i.e.,  $\text{M}^{2+}$  and two negatively charged rings), this approach is of some utility in interpreting electronic absorption spectra.

It must also be noted that not all  $(\text{C}_5\text{H}_5)_2\text{M}$  compounds are as simple structurally or electronically as might naively be expected. Those involving titanium and niobium have complex binuclear structures, as described in detail under the chemistry of these elements. In the case of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}$  there are two electrons in excess of those required for an 18-electron configuration; nonetheless, the molecule appears to have a structure with parallel rings and the two additional electrons have been assigned to the  $e_{1g}^*$  orbitals where they are appreciably delocalized onto the rings.

$(\text{C}_5\text{H}_5)_2\text{Mn}$  has a structure (Fig. 2-18) in which there are no discrete molecules until a transition occurs at  $159^\circ\text{C}$ , where it becomes isomorphous with ferrocene. However, there are five unpaired  $d$  electrons and the Mn to ring bonding is mainly ionic.  $(\text{CH}_3\text{C}_5\text{H}_4)_2\text{Mn}(\text{g})$  at  $25^\circ\text{C}$  is a roughly 2 to 1 mixture of ionic (high-spin) and covalent (low-spin) molecules with Mn—C distances of 2.42 and 2.14 Å, respectively, while  $(\text{C}_5\text{Me}_5)_2\text{Mn}$  is molecular with one unpaired electron.

In many cases the rings are not parallel because additional ligands are present, for example, in  $(\text{C}_5\text{H}_5)_2\text{MX}_2$  compounds with  $\text{M} = \text{Ti}, \text{Zr}, \text{Mo}$  and  $\text{X} = \text{Cl}, \text{H}$ , or  $\text{R}$ , or  $(\text{C}_5\text{H}_5)_2\text{MnPR}_3$ .<sup>34</sup> Bent molecules are also formed by tin and lead, where there is a stereochemically active lone pair.<sup>35</sup> Finally there

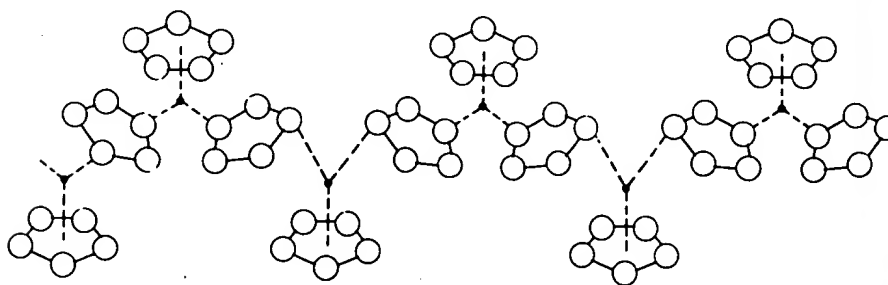


FIG. 2-18. The chain structure of  $(\text{C}_5\text{H}_5)_2\text{Mn}$  in the low-temperature, antiferromagnetic crystal form.

<sup>34</sup>G. Wilkinson *et al.*, *J. Am. Chem. Soc.*, 1984, 106, 2033.

<sup>35</sup>A. H. Cowley *et al.*, *J. Am. Chem. Soc.*, 1982, 104, 4064.

FIG. 2.  
orbitals

can be  
is pro

It is  
atom  
energy  
with th  
The C  
of bon

Bor  
examp  
symme  
only  $\pi$   
by met  
might  
is still

Journal  
Dötz, K.  
Hawkins  
1971.  
Martell,  
Volur  
Comy

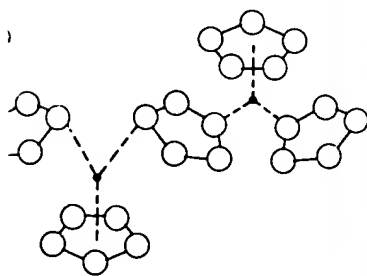
J. W. Fa  
1984, 3, 1

ple, the  $de_1$  orbitals, to form their

just given for ferrocene is *qual-*  
other  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds,  
 $(\eta\text{-arene})_2\text{M}$  molecules. Relative  
metal is changed. Ferrocene itself  
ulations, and at the other extreme  
l to the  $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds  
e to treat the bonding in these  
negatively charged rings), this  
electronic absorption spectra.  
 $(\eta\text{-C}_5\text{H}_5)_2\text{M}$  compounds are as simple  
ly be expected. Those involving  
structures, as described in detail  
the case of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ni}$  there are  
or an 18-electron configuration;  
structure with parallel rings and  
ed to the  $e_1^*$  orbitals where they

which there are no discrete mol-  
re it becomes isomorphous with  
 $d$  electrons and the Mn to ring  
25°C is a roughly 2 to 1 mixture  
molecules with Mn—C distances  
 $\text{Me}_3)_2\text{Mn}$  is molecular with one

because additional ligands are  
nds with  $\text{M} = \text{Ti}, \text{Zr}, \text{Mo}$  and  
molecules are also formed by tin  
active lone pair.<sup>35</sup> Finally there



temperature, antiferromagnetic crystal

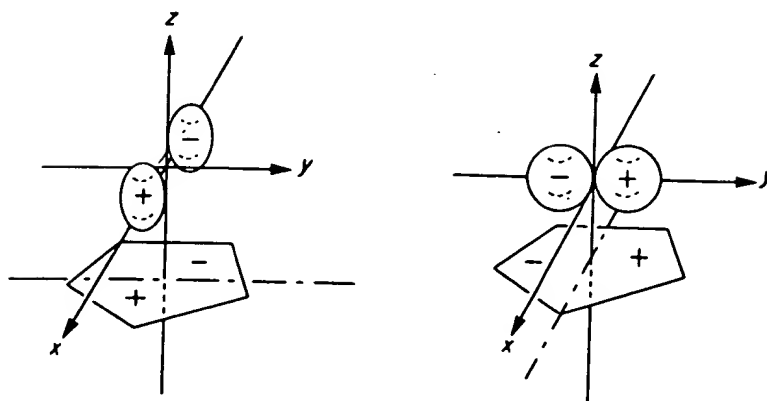


FIG. 2.19. Diagrams showing how  $p_x$  and  $p_y$  orbitals are symmetry adapted to overlap the  $e_1$   $\pi$  orbitals of a  $\text{C}_5\text{H}_5$  ring.

can be "slippage" of the metal from the center to one side of the ring, which is probably important in the conversion of  $\eta^5$  to  $\eta^1$  species (Section 26-10).<sup>36</sup>

It is also possible to have covalent  $(\eta\text{-C}_5\text{H}_5)\text{M}$  groups even when the metal atom has no valence shell  $d$  orbitals, provided it has  $p$  orbitals of suitable energy and size. As shown in Fig. 2-19, a pair of  $p_x$  and  $p_y$  orbitals can overlap with the  $e_1$   $\pi$  orbitals of  $\text{C}_5\text{H}_5$  in much the same way as do  $d_{xz}$  and  $d_{yz}$  orbitals. The  $\text{C}_5\text{H}_5\text{In}$  and  $\text{C}_5\text{H}_5\text{Tl}$  molecules are the best documented cases of this type of bonding.

**Bonding in  $(\eta\text{-C}_8\text{H}_8)_2\text{M}$  Molecules.** Although there are a few cases—for example,  $(\eta\text{-C}_8\text{H}_8)\text{ZrCl}_2(\text{THF})$ —of one fully octagonal, planar  $\text{C}_8\text{H}_8$  ring being symmetrically bonded to a  $d$ -block metal and it may be safely assumed that only metal  $d$  orbitals are used, the  $(\eta\text{-C}_8\text{H}_8)_2\text{M}$  compounds are formed only by metal atoms like uranium and thorium where the participation of  $f$  orbitals might reasonably be expected. However, at present, the role of the  $f$  orbitals is still not well defined. See Section 21-7 for further discussion and references.

### General References

- Journal of Inclusion Phenomena*, Vol. 1, 1983, D. Reidel, Dordrecht.  
Dötz, K. H. et al., *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, 1983.  
Hawkins, C. J., *Absolute Configuration of Metal Complexes*, Wiley-Interscience, New York, 1971.  
Martell, A. E. and R. M. Smith. *Critical Stability Constants*, Volume 1: *Amino Acids*, 1974, Volume 2: *Amines*, 1975, Volume 3: *Other Organic Ligands*, 1977, Volume 4: *Inorganic Complexes*, 1976, Volume 5: *First Supplement*, 1982, Plenum Press, New York.

<sup>35</sup>J. W. Faller et al., *Organometallics*, 1985, 4, 929; D. L. Lichtenberger et al., *Organometallics*, 1984, 3, 1614, 1623.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**